



NASA CR-54170
MRB5007Q2

FACILITY FORM 802
N64-30605
(ACCESSION NUMBER)
99
(PAGES)
Or-54170
(NASA CR OR TMX OR AD NUMBER)

(THRU)
1
(CODE)
06
(CATEGORY)

Quarterly Report No. 2

STUDY OF FUEL CELLS USING STORABLE
ROCKET PROPELLANTS

28 April to 27 July 1964

by

J. C. Orth, R. E. Chute, R. Havlin, K. W. Klunder,
S. Matsuda, W. H. Power, and J. O. Smith

prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

CONTRACT NAS 3-4175

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25 September 1964

CONTRACT NAS 3-4175

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SUMMARY

Porous anodes and cathodes utilizing porous Teflon vapor diffusion barriers were demonstrated. The hydrophobic porous Teflon membrane, in contact with the fuel or oxidant, prevented wetting of the electrode from the reactant storage side. Reactant vapor passed through the porous Teflon membrane and into the catalyzed porous conductor electrode where it was anodically oxidized or cathodically reduced. The Teflon barrier was designed to separate the electrolyte from the concentrated reactants, allowing the transport of only reactant vapor to the electrode-electrolyte-catalyst interface. The limiting cell current was controlled by the vapor pressure of the reactant, the porosity and thickness of the Teflon barrier, and the Teflon bonding procedure. Limiting currents of 100 ma/cm² were obtained consistently with 15 mil thick, 19 μ pore size Teflon sheet.

The bonding of porous Teflon sheets to porous carbon electrodes at 350°C reduced the diffusion rate of HNO₃ at 90°C by a factor of 20 for 19 μ pore size and 25 mil thick Teflon sheet.

The utilization of flow-through electrodes in an operating fuel cell using soluble fuels and oxidants requires that the cell operate with reasonable contamination levels of fuel and oxidant in the electrolyte. A N₂H₄ anode, for instance, must not be adversely affected by contact with small concentrations of an oxidizing agent, and a HNO₃ cathode should be stable in contact with small concentrations of hydrazine that have leaked through the anode without reacting. Pure carbon cathodes were found to be selective in 5M H₃PO₄ at 90°C for the cathodic reduction of HNO₃ in the presence of 0.5M N₂H₄ and Pt-containing anodes were selective for the oxidation of N₂H₄ in the presence of 1M HNO₃. Deterioration of performance for these contamination levels are 0.15 V and 0.20 V at 100 ma/cm² for HNO₃ and N₂H₄ electrodes, respectively. Electroplated Pt showed better activity than chemically reduced Pt on FC-13 carbon substrate.

Diffusion electrodes prepared by bonding 6 mg/cm² of Teflon powder to FC-14 carbon allowed a HNO₃ diffusion rate sufficient to support 100 to 200 ma/cm² at 0.90 to 0.95 V vs. SHE. The steady state contamination level of HNO₃ in the electrolyte with this cathode was only 0.04M HNO₃.

Full cells with 9-in.² electrodes and cation exchange membranes have been evaluated for the system HNO₃/N₂H₄ in KOH. Appreciable electrical output was obtained, but life was limited by HNO₃ attack on the membranes.

Life of cation exchange membranes was extended from about 8 hours to at least 70 hours by use of a porous buffer layer containing neutralization by-products between the HNO₃ cathode and the membrane. A current density of 70 ma/cm² was produced at 1.1 V and 70°C.

A zirconium phosphate ion exchange separator was fabricated and tested in an acid/base fuel cell.

Construction of an experimental catalytic reformer for the decomposition of monomethyl hydrazine (MMH) was started. The design of the reformer essentially followed that given in the project proposal of 10 February 1964. A literature study of hydrazine decomposition and MMH reactions was undertaken.

The effect of a third element either as an alloying species or as a surface oxide on the electrode performance of the Pd-25% Ag diffusion electrode was studied. The study was used mainly for screening purposes to determine the most active catalysts for the hydrogen diffusion electrode. The data also suggested a correlation of the catalytic activity of these metal oxides with the periodicity of the elements. Selected activated electrodes were tested as anodes under severe polarization for periods of up to two weeks.

The best Pd-Ag electrodes were prepared by annealing them at 850°C in an argon atmosphere, plating with Rh black, oxidizing in pure O₂ gas at 850°C, and subsequently oxidizing at 700°C. These electrodes carried 250 ma/cm² at a steady overpotential of about 0.50 v vs HE for two weeks.

The optimum conditions for Rh black plating was 1 to 4 mg/cm² from 0.01M RhCl₃ of pH 1 at a cathodic current density of about 125 ma/cm².

Palladium hydrogen diffusion electrodes that were oxidized in pure oxygen showed better anodic activity for hydrogen oxidation than those treated in air, perhaps because of an increase in cation vacancy sites and the quantity of rhodium oxide. However, oxidation in an atmosphere containing SO₂ gas or in pure SO₂ poisoned the electrodes despite the assumption that SO₂ addition might increase the number of cation vacancies.

Tests on Pd-25% Ag foil alloyed with 10% Pt showed almost identical properties as a hydrogen diffusion anode as Pd-25% Ag foil. Since this ternary alloy has better resistance than the Pd-25% Ag foil to attack by oxidizing acids such as HNO₃, the use of the Pd-Ag-Pt alloy should be considered for systems that use strongly oxidizing acids as cathode reactants.

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I. INTRODUCTION

The objective of this program is to develop a fuel cell operating on storable reactants and to design a fuel cell that will operate relatively efficiently on a variety of fuels and oxidants.

The last quarterly report described initial designs of 3 by 3 in. full cells with nickel plaque cathodes and hydrogen diffusion anodes. Another full cell with a porous Teflon hydrazine cathode and an oxygen or hydrogen peroxide cathode was constructed and tested. Although good current densities (100 ma/cm^2) and reasonable voltages were attained for short-term testing, the electrodes failed after several hours' discharge. Solid Pd hydrogen diffusion electrodes were demonstrated for the use of 85% $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ as the fuel with 5M H_2SO_4 electrolyte. Reproducible anodic polarization curves for Pd-25% Ag hydrogen diffusion electrodes were obtained only after controlled oxidation of the surface of the foil.

The Pd-25% Ag electrode was activated by oxidation, and the activation was further increased by rhodium black plating before oxidation. The catalytic action produced by oxidation was attributed to the thin oxide film, which is a p-type semiconductor (cation vacancy type). Heating foils in a hydrogen atmosphere degraded the electrodes by reducing the PdO catalytic film.

The use of a solid Pd membrane as a hydrogen diffusion anode with hydrazine as a fuel was demonstrated in anhydrous HF solution ($\text{KF} \cdot 3\text{HF}$) at 85°C . Porous Ni plaque was also demonstrated as a flow-through electrode in anhydrous HF.

During this quarter, development continued on the porous Teflon vapor diffusion electrode. Limiting diffusion rates of reactants through the electrode were evaluated, and the steady state contamination level of reactant in the electrolyte was determined. Selective catalysts for both the cathodic reduction of HNO_3 and the anodic oxidation of N_2H_4 were selected. Several full cell systems were built and tested. A monomethylhydrazine catalytic reformer was constructed.

Studies of Pd solid diffusion electrodes presented in this report include the effect of additional alloying elements on activation of the Pd-Ag system for use as a hydrogen anode. Metallographic and electron microprobe analyses on the cross sections of these foils were made to determine the structure of the electrodes, particularly of the diffusion layer. The Pt-Pd-Ag alloy was evaluated as a hydrogen diffusion anode, and several procedures for activating electrodes by alloying and oxidation were devised. Data relating alloying elements to electrode activation were arranged according to the periodicity of the alloying elements to determine if general periodic trends could be uncovered.

II. POROUS TEFLON VAPOR DIFFUSION ELECTRODES

A. BACKGROUND

The overall objective of this phase is to develop anode and cathode half cells that have the physical, chemical, and electrochemical attributes to allow direct scale-up for use in 3 by 3 in. full cells with acid electrolyte. Both HNO_3 and N_2O_4 are oxidizer candidates; N_2H_4 is the fuel. This objective requires both basic electrochemical studies and the construction and testing of full cells. Accordingly, cathode development has required a study of porous Teflon diffusion control variables. Since we have previously found that a suitable catalyst for HNO_3 reduction is carbon*, further investigations are oriented toward testing types of construction that will be usable in a 3 by 3 in. cell and determining the maximum contamination levels that the electrodes can tolerate.

Anode development has been concerned with finding a suitable catalyst for the anodic oxidation of N_2H_4 , particularly in the presence of contaminant HNO_3 from cathode leakage. Semi-selective platinum electrodes for N_2H_4 oxidation in the presence of appreciable concentrations of HNO_3 are also desired.

The principal operating advantages of the vapor diffusion electrode are:

- (1) Storage of concentrated liquid reactants in a back-side container adjacent to a non-wettable Teflon barrier.
- (2) Diffusion of vapor from this concentrated source through the porous Teflon barrier to the catalyst area. The diffusion rate may be regulated by the vapor pressure of the concentrated source or the thickness of the porous barrier.
- (3) Tolerance of significant contamination of fuel (or oxidant) by a semi-selective cathode (or anode) catalyst, while limiting the contamination of electrolyte by both reactants to a tolerable concentration.
- (4) Use of this development with other fuel and oxidant gases or liquid systems that do not wet the Teflon porous film.

* FC-13 or FC-14, Pure Carbon Company, St. Marys, Pennsylvania.

B. CATHODE DEVELOPMENT

1. Cathodes Utilizing Porous Teflon Diffusion Barriers

a. Types of Construction

(1) Carbon-Teflon Powder Mixture Pressed into Porous Teflon Sheet

The electrode structure consisted of a tantalum ring holder, a porous Teflon controlling sheet, and the pressed powder mixture of carbon and Teflon powder with a tantalum screen current collector (see reference 1 for general preparation details).

(a) Variation of Activity with Teflon Loading

The most significant trend noted in the carbon-Teflon powder electrodes is the variation of polarization characteristics with Teflon loading. Voltammetric curves for the reduction of 70% HNO_3 and N_2O_4 (1 atm) with Teflon loadings from 0 to 50 mg/cm^2 are shown in Figure 1. The lower Teflon loadings resulted in better electrochemical performance.

(b) Resistance and Reproducibility of Electrode

The carbon-Teflon powder electrodes have been plagued by both erratic and high internal electrode resistance and the difficulty of preventing gross leakage of oxidant around the edges of the electrode. The erratic resistance was attributed to the tantalum screen current collector. Some attempts were made to eliminate this source of resistance by substituting gold plated screens. This proved futile because of a permanent high resistance of the Teflon-carbon mixture.

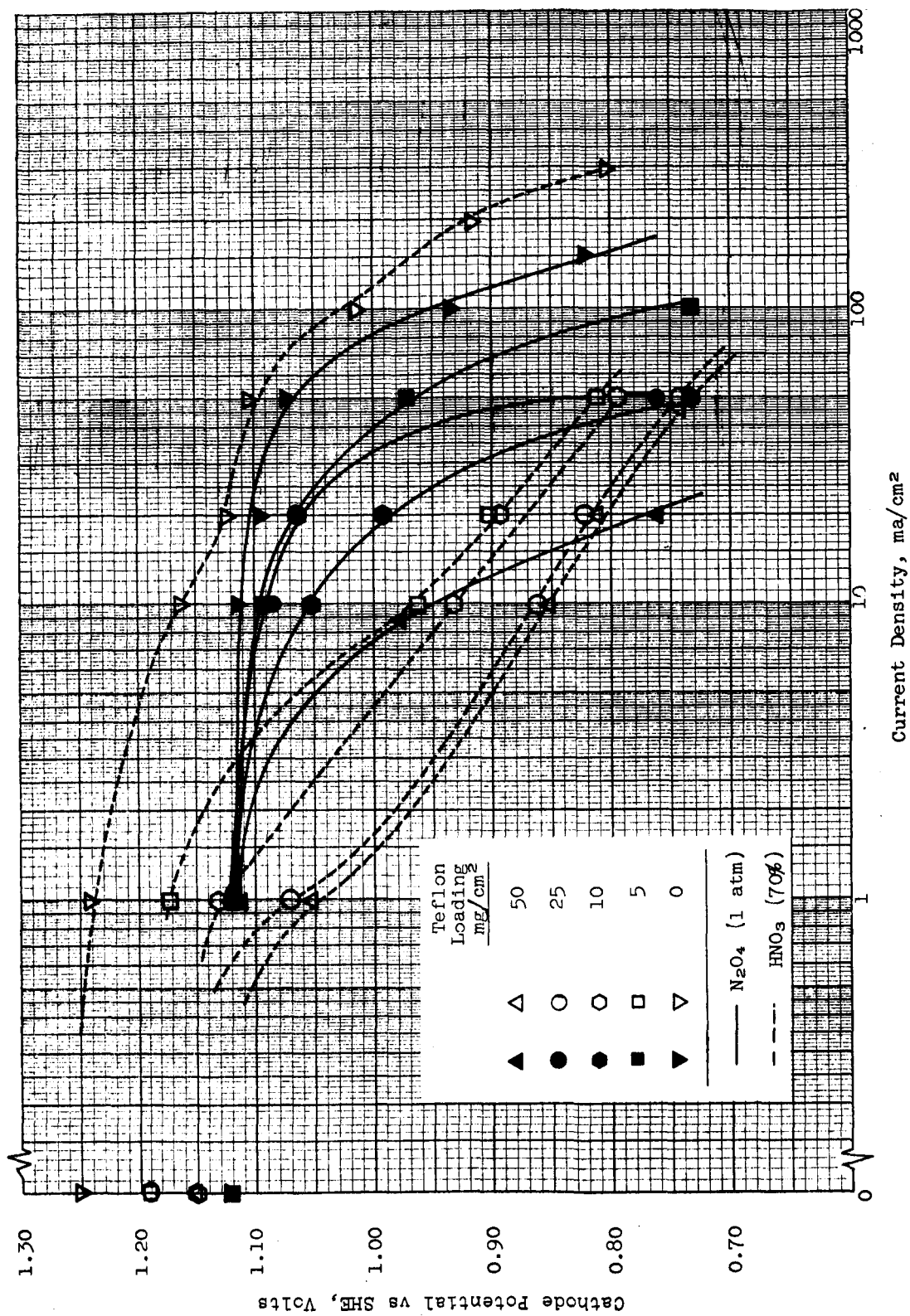
At very low Teflon loadings, lower resistances could be realized in most cases. However, the physical stability of the electrodes was poor at low Teflon loadings.

(c) Conclusions

Alternate types of construction were indicated because of the resistance and reproducibility difficulties mentioned above.

(2) Solid Carbon Insert in Tantalum Holder

This type of construction utilized a carbon circle slightly smaller than the opening of a standard tantalum holder. The total assembly, including tantalum mesh to give a tight fit between the holder and the carbon, was pressed at 350°C to bond the Teflon diffusion barrier to the carbon. Erratic electrode resistances were present, presumably because of a non-reproducible contact between holder,



Current Density, ma/cm²

Construction Pressure: 4000 lb/in²

Construction Temperature: 350°C

Electrolyte: 5M H_2SO_4

Catalyst: Shawinigan Black 25 mg/cm²

Cell Temperature: 90°C, 19 micron 0.015-in. thick porous Teflon

Figure 1. Effect of Teflon-Carbon Ratio on Cathodic Polarization

mesh, and carbon. When sufficient pressure was used to insure good contact, mechanical failure of both carbon and Teflon barriers resulted in gross leakage through the electrode.

When construction conditions were well controlled, the performance of the solid carbon insert electrode was quite good. Polarization curves for FC-13 and FC-14 carbons with 70% HNO_3 and N_2O_4 (1 atm) in 5M H_2SO_4 electrolyte are shown in Figure 2. The polarization is nearly all IR drop up to a current density of 150 ma/cm² where concentration polarization begins to limit the electrode performance. If the IR drop is eliminated from the potentials at 100 ma/cm², the potentials are 1.09 to 1.14 v vs SHE. These excellent IR-free polarization curves indicate that the use of a diffusion barrier bonded to the solid carbon structure has the necessary electrochemical characteristics for the cathodic reduction of HNO_3 and N_2O_4 . Therefore, modified constructions that eliminated the erratic resistance features of the first carbon-Teflon electrode types were designed.

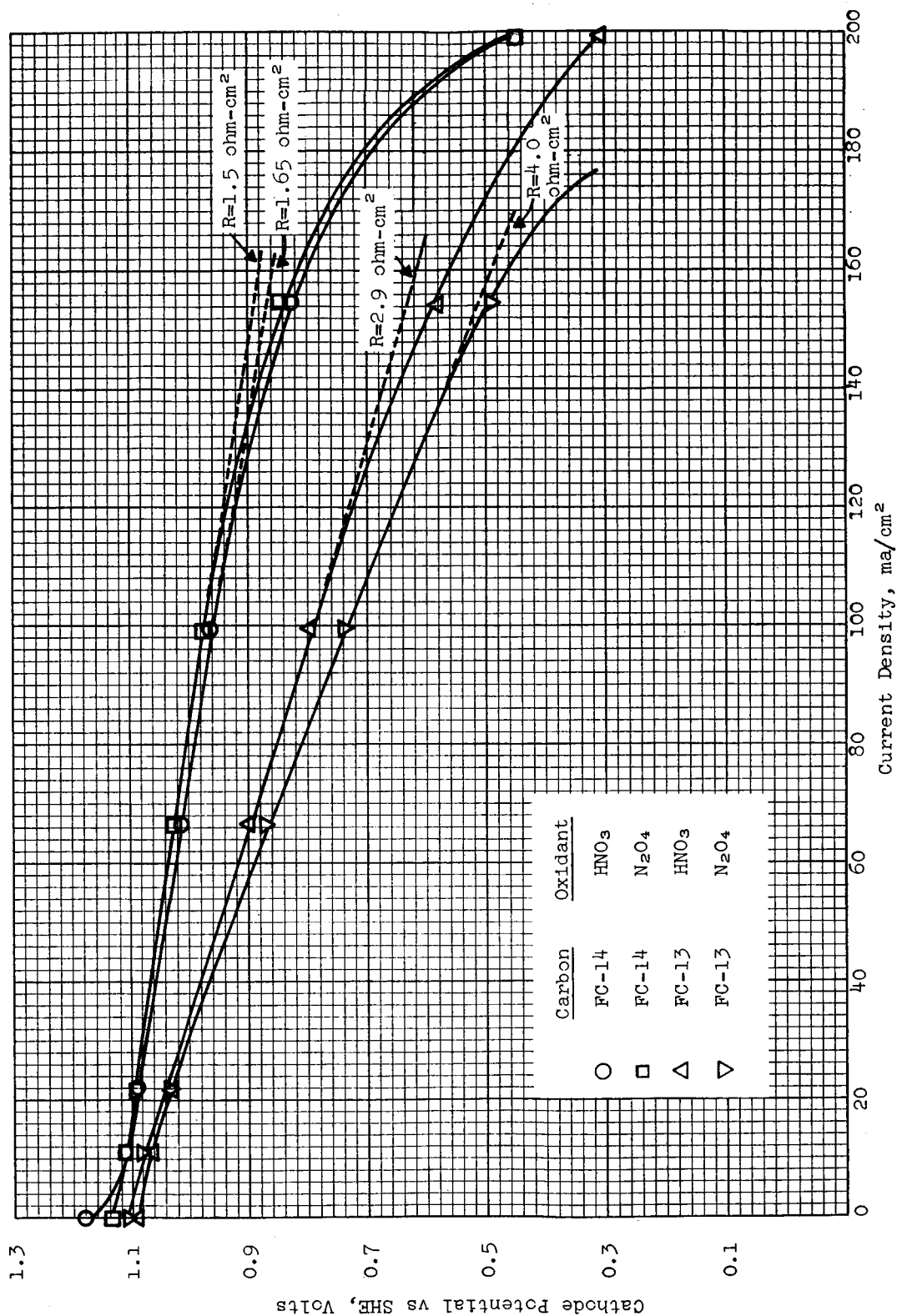
(3) Low Resistance Solid Carbon-Teflon Diffusion Electrodes

(a) One-Piece Carbon Construction with Polystyrene Sealant

Because of the difficulties mentioned above with the tantalum holder construction, a one-piece assembly of carbon with a sealed outer region to prevent leakage was tested. To seal those porous areas outside the O-ring, polystyrene was applied from a benzene solution, and the benzene was removed by vacuum evaporation. Electrical contact was made by copper clips attached before applying the polystyrene. This construction gave low, reproducible electrode resistances and the corresponding reproducible potential-current curves for the cathodic reduction of HNO_3 as shown in Figure 3.

(b) Two-Piece Carbon Construction with Shrink-Fit Contacts

Although the one-piece construction mentioned above is satisfactory for preliminary testing, the use of polystyrene as a sealant necessarily adds an impurity to the electrode that is subject to attack by the cell reactants and also results in an ill-defined active electrode area. Thus, while testing with the one-piece construction was under way, the Pure Carbon Company has custom-fabricated a two-piece carbon electrode. The construction features, shown in Figure 4, include a thermally made, non-leakage bond between an active catalytic inner carbon and an impervious outer carbon. This system needs no further waterproofing and insures an exact knowledge of the active electrode area.



Electrolyte: 5M H_2SO_4
 Oxidants: 70% HNO_3 or N_2O_4 (1 atm)
 Extrapolated Linear Curve
 (Voltage drop on this curve represents IR drop only)

Figure 2. Cathodic Polarization of Solid Carbon and Porous Teflon Electrodes

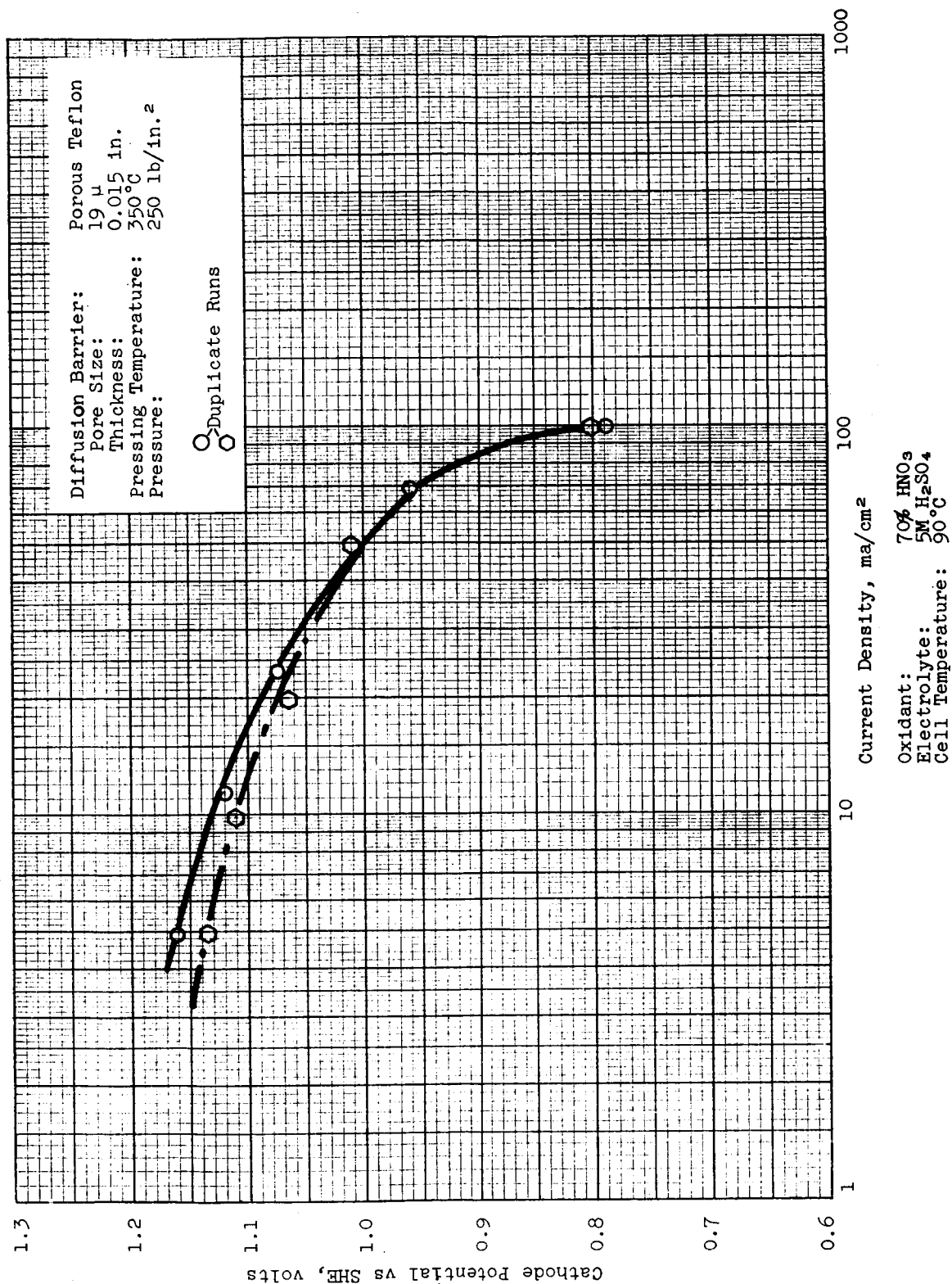


Figure 3. Cathodic Reduction of HNO₃ at One-Piece Carbon Electrodes

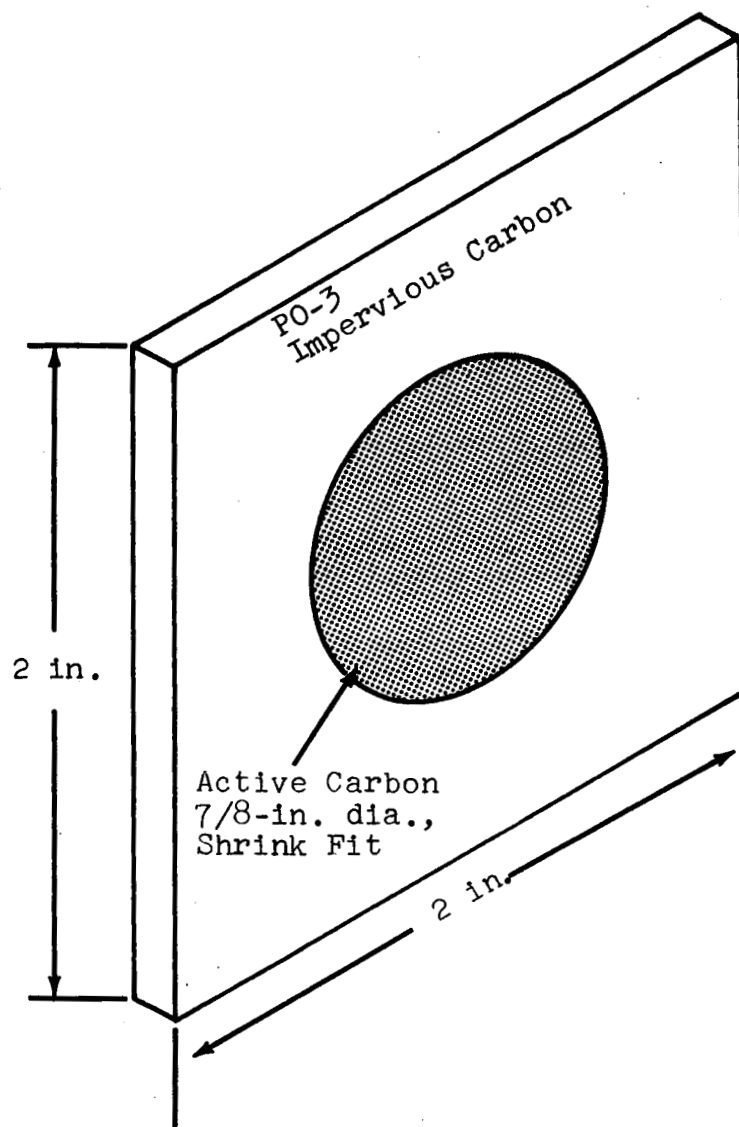


Figure 4. Dual Carbon Electrode

b. Carbon Selectivity to HNO₃ Reduction

(1) Background

Last year's final report (ref. 1) stated that 5M HNO₃ was not reduced by 1M N₂H₄ when the two solutions were mixed and heated at 90°C. The salt formation reaction between the acid and base, forming N₂H₅NO₃ apparently precludes redox reaction as in the formation of NH₄NO₃ from NH₃ and HNO₃. A mixture of HNO₃ and N₂H₄ might therefore be used as a combination electrolyte, oxidant, and reductant if a cathode could be devised that were sensitive only to reduction reactions for HNO₃ and if an anode is found that were selective for the oxidation of N₂H₄. We have previously found that carbon possesses not only an excellent catalytic activity toward HNO₃ reduction but also has a certain selectivity for HNO₃ in the presence of N₂H₄. Further work was believed justified to determine if this selectivity is active during diffusion-controlled experiments.

(2) Results

Cathodic polarization curves for HNO₃ reduction at porous carbon-Teflon diffusion electrodes are shown in Figure 5. The best curve was obtained with no electrolyte (5M H₃PO₄) contamination. Contamination of the electrolyte with 0.5M N₂H₄ and 3M HNO₃ resulted in lower potentials up to a current density of about 80 ma/cm². At higher current densities the presence of 3M HNO₃ in the electrolyte resulted in a better cathodic potential than that of a cathode in contact with uncontaminated 5M H₃PO₄. The presence of only 0.5M N₂H₄ contaminant in the electrolyte decreased the cathodic reduction potential of the porous Teflon-carbon electrode by 0.17 v at 70 ma/cm², but the electrode still operated as a cathode at this reasonable current density. This behavior is typical of the selectivity of all such electrodes regardless of diffusion limitations.

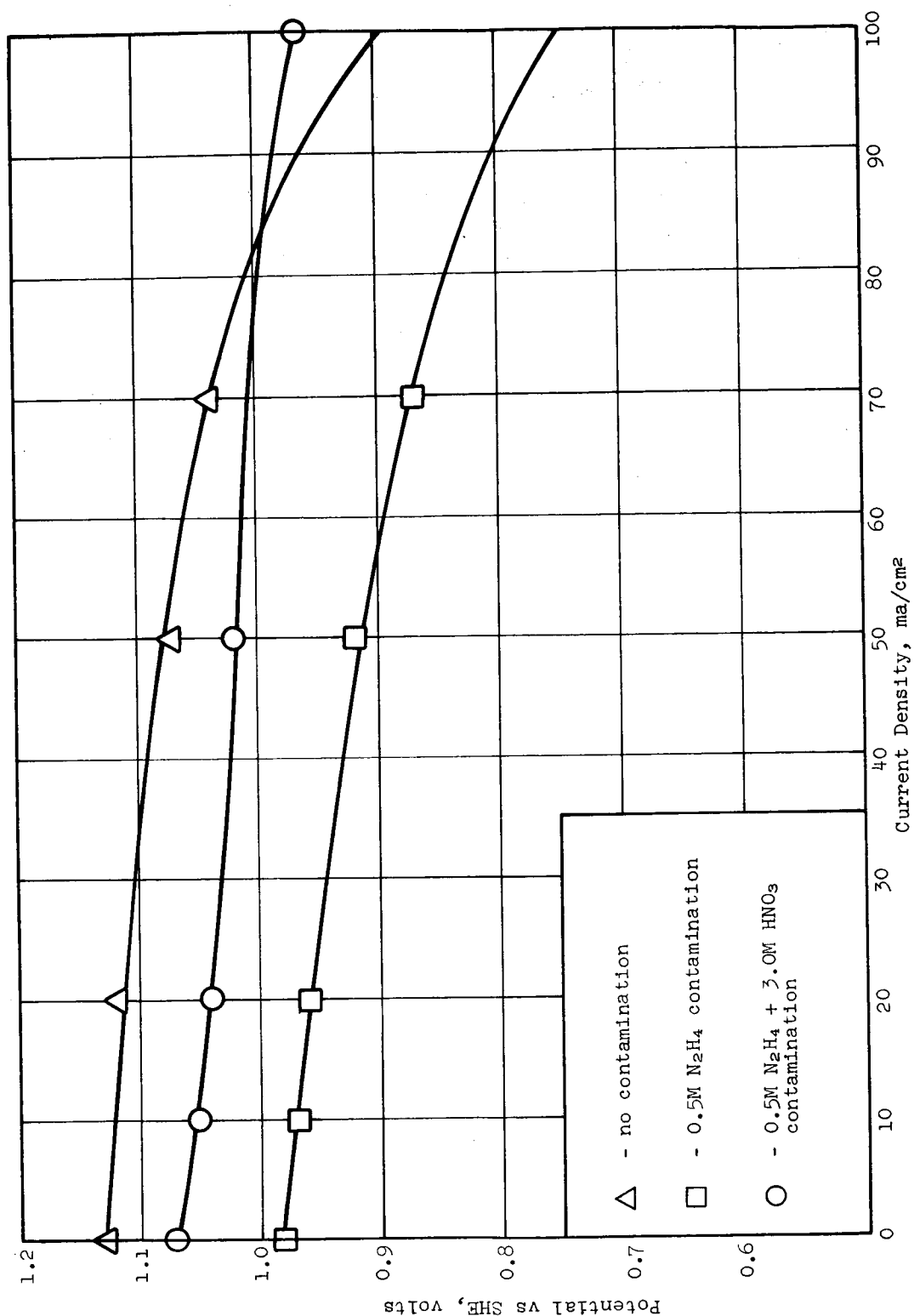
2. Role of Porous Teflon Sheet in Diffusion Control

a. Background

Variables inherent in the use of porous Teflon sheet as a diffusion control medium are pore size, effective pore length, porosity, and character of the carbon-Teflon bonding.

Gas diffusion equations invariably stem from a form of Fick's Law:

$$N = -D_m A \frac{dc}{dL} \quad (\text{ref. 2}) \quad (1)$$



Temp. 90°C, Electrolyte 5M H₃PO₄. Porous Teflon 194, 0.009-in. thick

Figure 5. Selectivity of Carbon Cathodes for HNO₃ Reduction in Contaminated Solutions

where N = moles/unit time
 D_m = molal diffusion coefficient
 A = diffusion area
 L = effective pore length
 c = concentration
 $\frac{dc}{dL}$ = concentration gradient

Assuming a linear gradient, this integrates to:

$$N = \frac{D_m A (c_1 - c_2)}{L} \quad (2)$$

The porosity fraction, p , can be calculated from the true density, d_t , and the apparent density, d_a , of the electrode material:

$$p = \frac{d_a}{d_t} \quad (3)$$

The effective diffusion area, then, is:

$$A = \frac{pV}{L} \quad (4)$$

where V is the geometric electrode volume. If the pore length is the same as the electrode thickness, all terms of Equation 4 are constant. However, if the pore length depends on its tortuosity, the diffusion rate becomes:

$$N = \frac{D_m p V (c_1 - c_2)}{L^2} \quad (5)$$

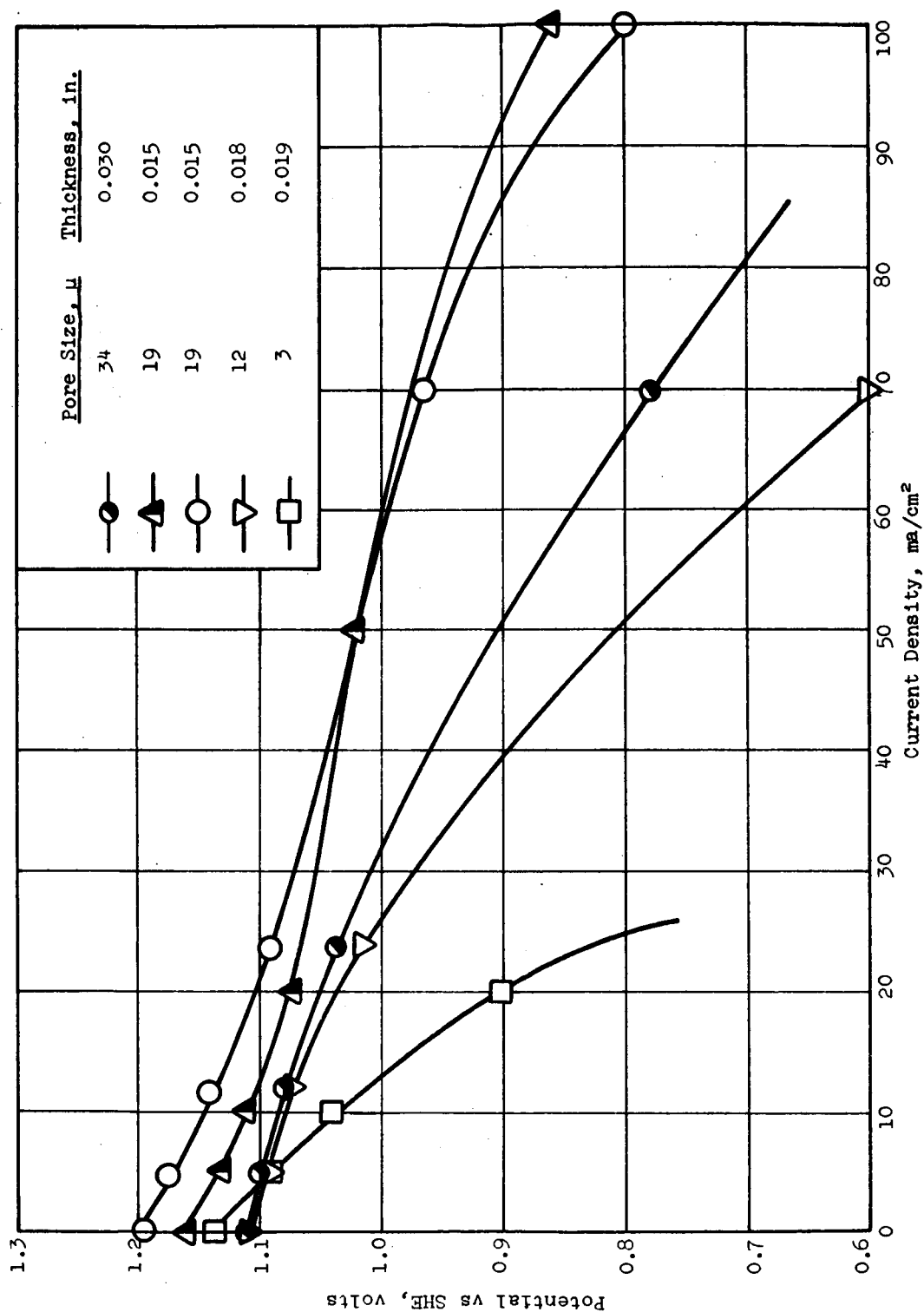
b. Effect of Variables of Teflon Electrode on Electrochemical Characteristics

(1) Pore Size

The cathodic polarization characteristics were measured for electrodes that were made by pressing porous Teflon with four different pore sizes against solid FC-14 carbon. The polarization data, presented in Figures 6 and 7, show a distinct trend with pore size. The limiting current density (and diffusion rate) of HNO_3 increases with increasing pore diameter for electrodes that are normalized for thickness.

(2) Thickness

The dependence of diffusion rate upon thickness is clearly shown by the reversal of the pore size trend by 30-mil thick 34- μ pore diameter Teflon sheet (Figures 6 and 7). However, attempts to find a more definitive relation by sanding Teflon samples to 9 to 11 mils thickness showed only small gains in the diffusion rate.



Electrolyte 5M H_2SO_4 at 90°C

Figure 6. Variation of N_2O_4 (1 atm) Cathodic Polarization Characteristics with Pore Size of Teflon Diffusion Electrodes

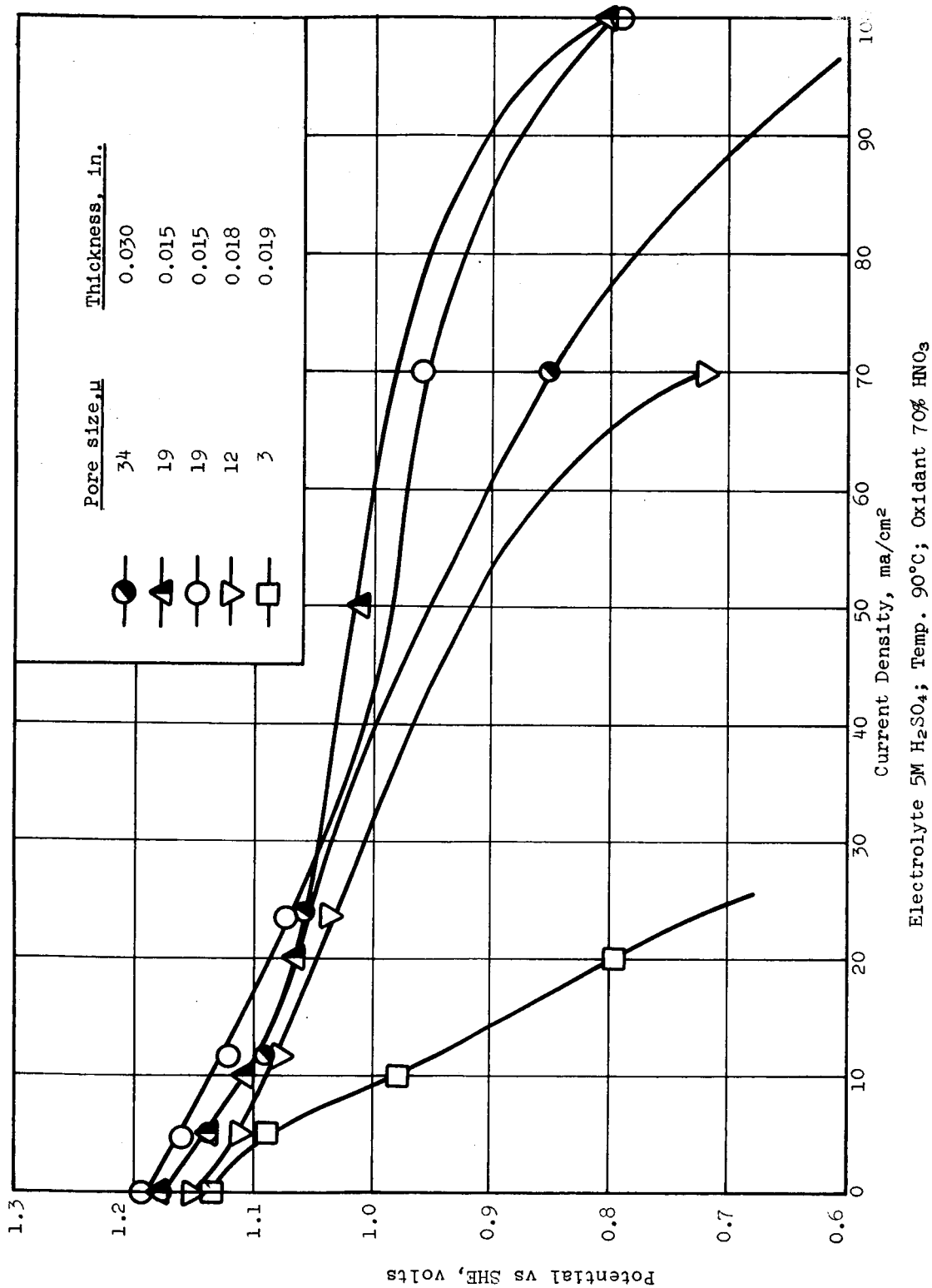


Figure 7. Variation of HNO₃ Cathodic Polarization Characteristics with Pore Size and Thickness of Teflon Diffusion Electrodes

Unsanded Teflon diffusion electrodes with pore size of 19μ , 12μ , and 34μ are compared with the respective sanded, thinner electrodes in Figures 8, 9, and 10. The sanded sides of the Teflon sheets were bonded to the carbon for some tests, and the unsanded sides were bonded in other tests. In all cases, the sanded side when bonded provided lower diffusion rates than the same Teflon sheet with the non-sanded side bonded. The diffusion rate of HNO_3 remained constant or increased with decreasing thickness of Teflon with the non-sanded side bonded. With 34μ and 12μ porous Teflon sheet having thickness of 8 and 20 mils, the sanded samples showed greater diffusion rates than the unsanded samples. The limiting current density was not strictly inversely proportional to the thickness (as Fick's law would indicate). The bonding operation at 350°C [above the melting point (327°C) of Teflon sheet] no doubt caused distortion and plugging of Teflon pores.

(3) Carbon-Teflon Bond

The nature of the Teflon surface when bonded to the carbon substrate had a large and consistent effect on the diffusion rate of oxidants through the electrode (Figures 8, 9, and 10). The greatest polarization improvement with sanding occurred for 12μ pore size Teflon sheet that was decreased in thickness by a factor of 2, while the 34μ pore size sheet was decreased in thickness by sanding by a factor of 3. This suggests that either the effect of bonding is less significant in the smaller pore sizes than in the larger pore sizes, or that the sanding process has less effect in plugging smaller pores.

Because of the results of the sanding tests, it was felt that an investigation of the effect of both heating and bonding on the diffusion rate of porous Teflon electrodes was needed. A method of measuring the diffusion rate of vapor from 70% HNO_3 through a porous Teflon electrode and into concentrated NaOH was devised. At intervals of 1, 3.25, and 6.5 hours, samples of the NaOH were taken and titrated with standard acid to obtain the amount of diffused HNO_3 vapor. From these data, an equivalent diffusion current for HNO_3 vapor was calculated, assuming the end product of the cathodic reduction to be NO .

Samples of 25-mil thick, 19μ pore diameter porous Teflon sheet in the untreated state, heat treated only at 350°C , and bonded at 350°C (bonded sample obtained by pressing porous sheet on carbon block at 350°C , then stripping from carbon) were tested at both 30°C and 90°C . These data are plotted in Figure 11. A certain time lag for reaching the maximum diffusion rate is apparent. However, very little change is noted between 3.25 and 6.5 hours.

At 90°C , the equivalent current density with the untreated Teflon sheet is nearly 3 times greater than that with the heat treated sample and about 20 times greater than that with the bonded sample.

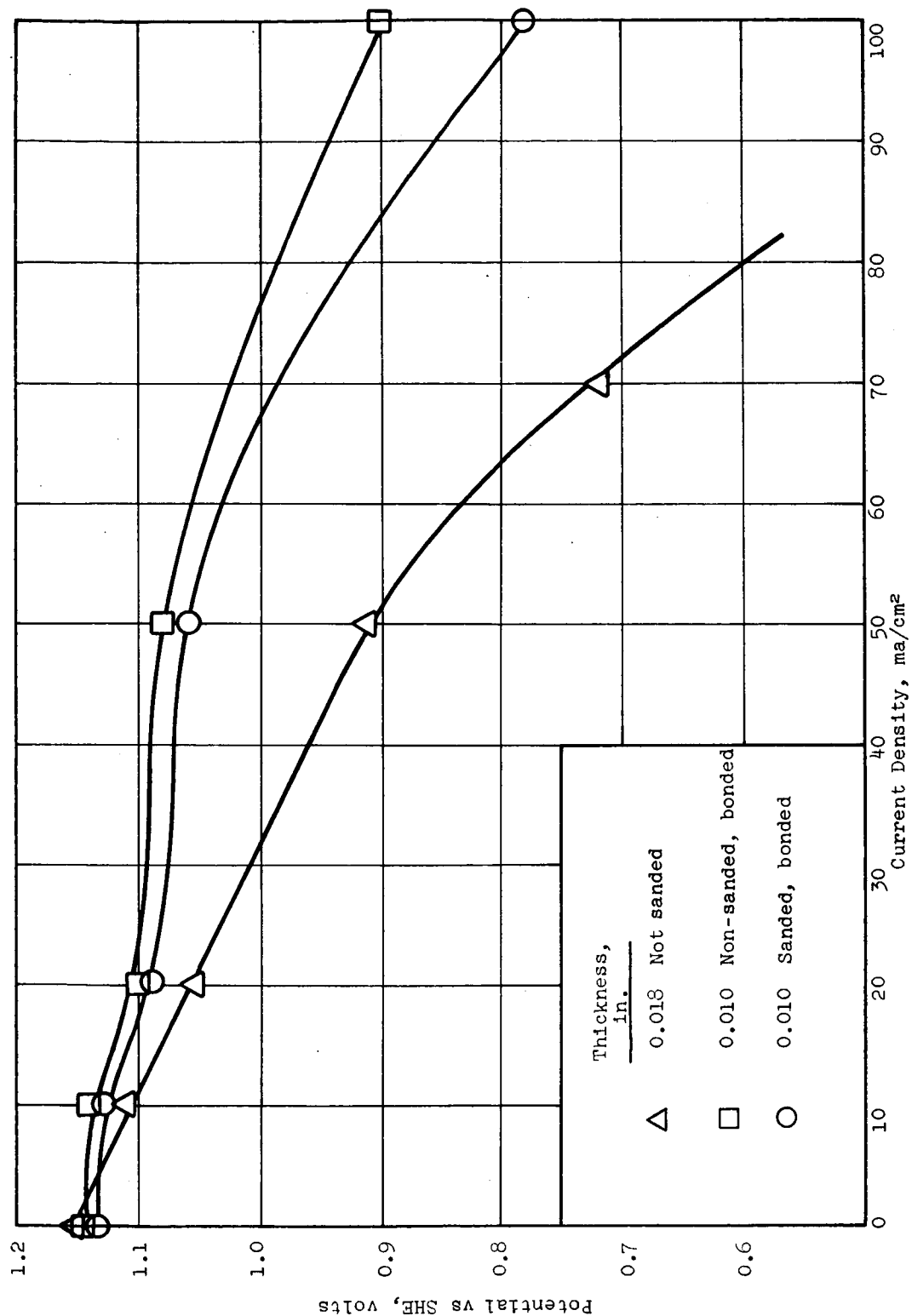


Figure 8. Effect of Thickness of 12 μ Porous Teflon Diffusion Electrodes on HNO₃ Cathodic Polarization Characteristics

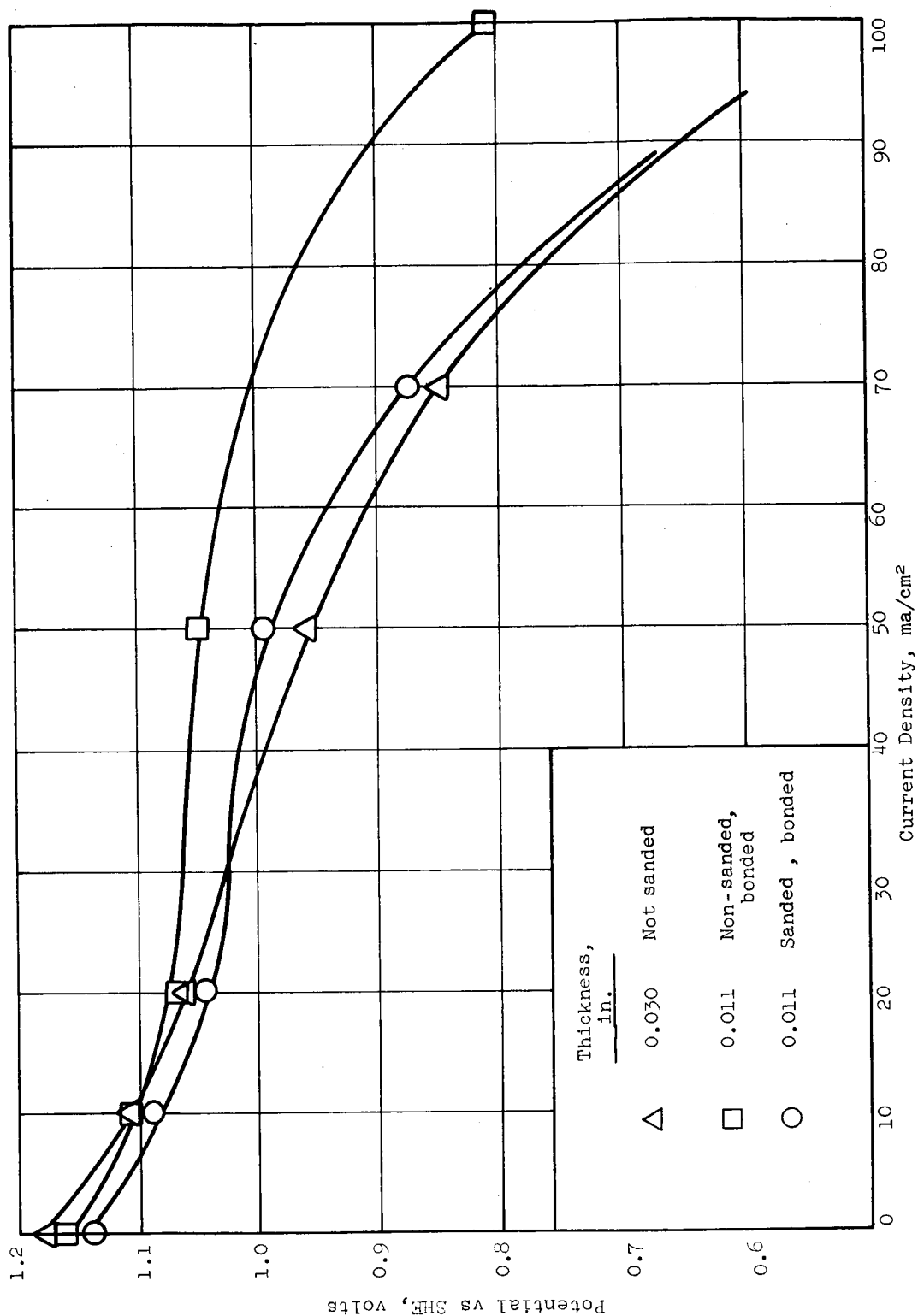


Figure 9. Effect of Thickness of 34μ Porous Teflon Diffusion Electrodes on HNO₃ Cathodic Polarization Characteristics

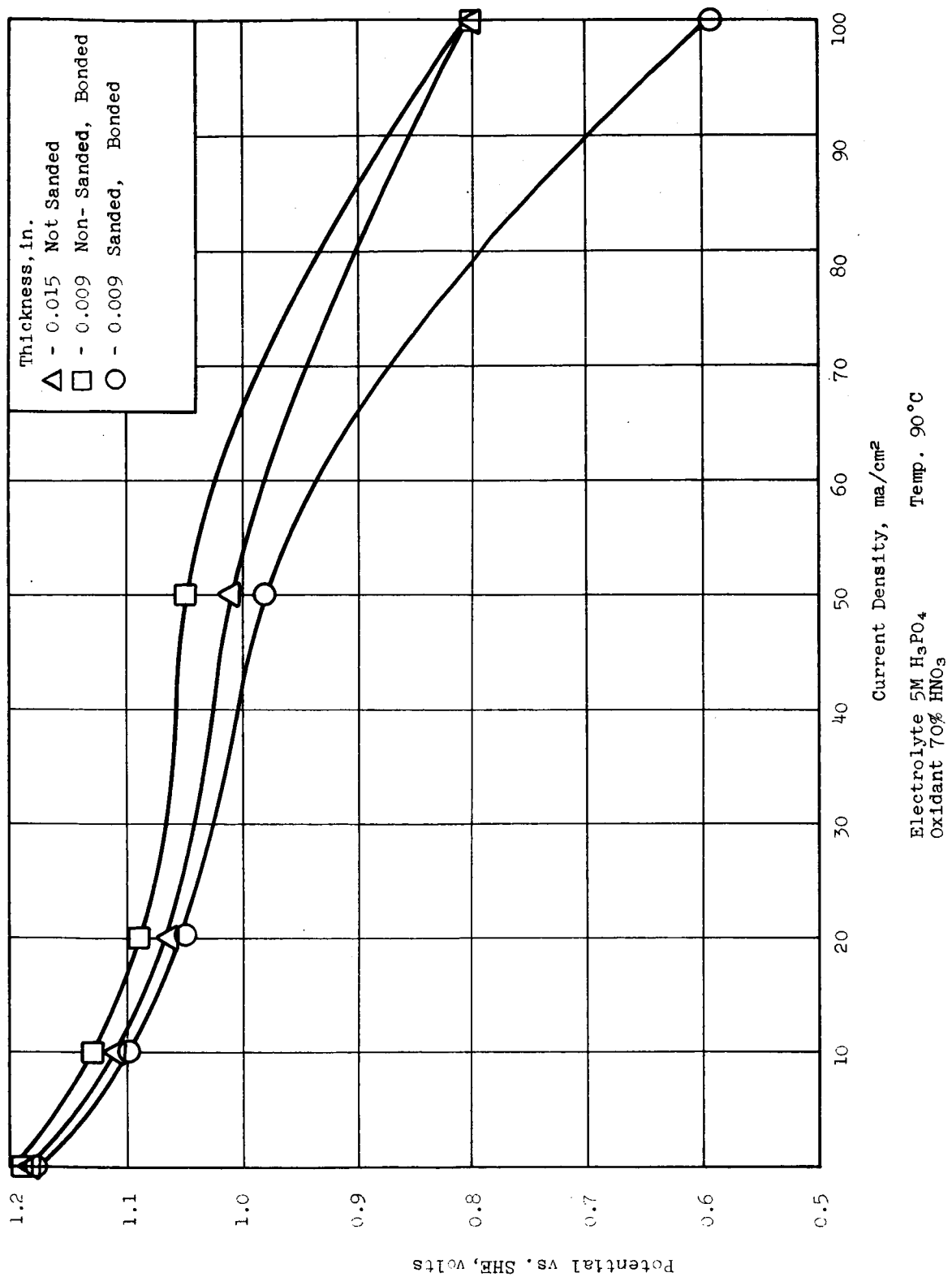
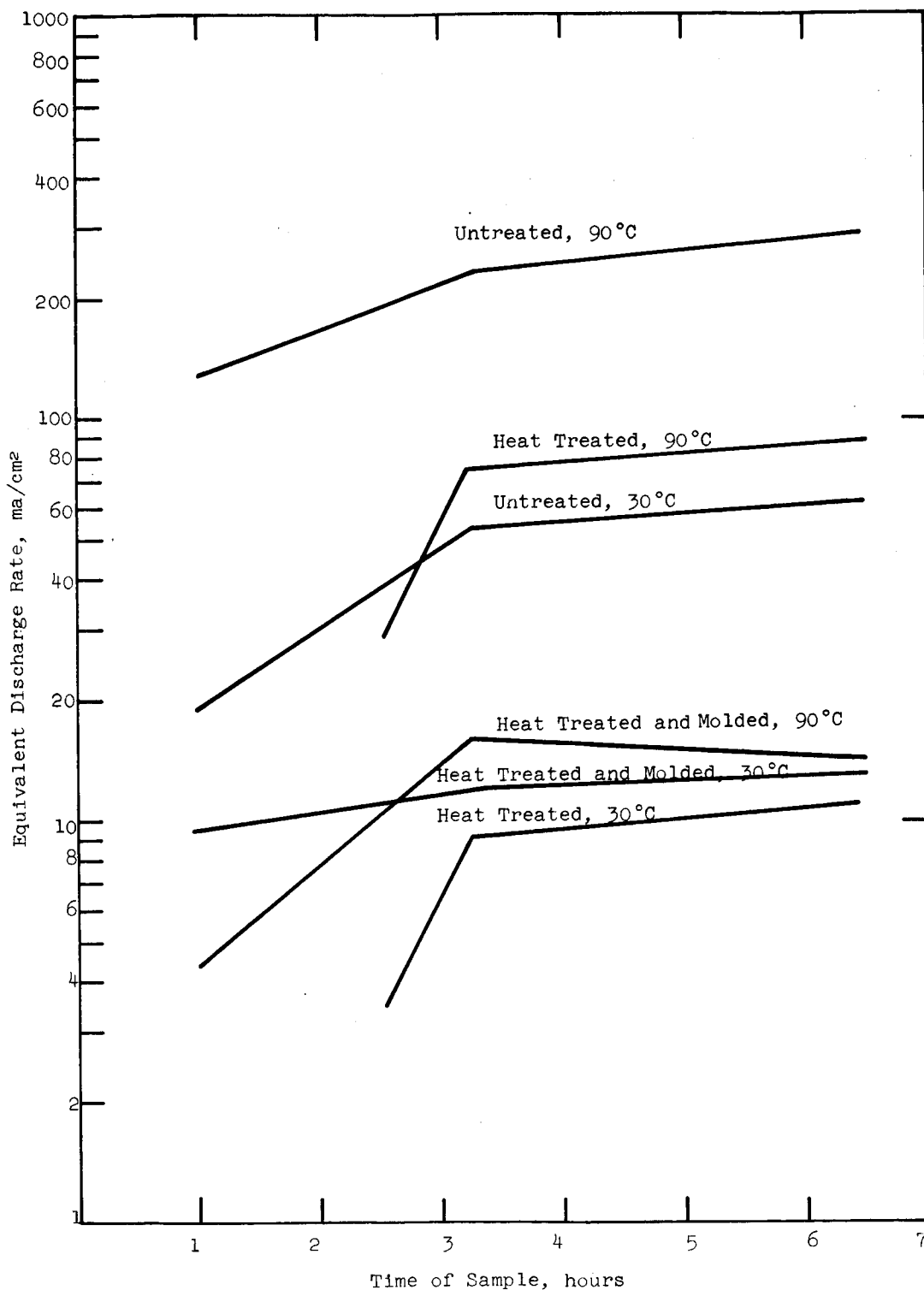


Figure 10. Effect of Thickness of 19 μ Porous Teflon Diffusion Electrodes on HNO₃ Cathodic Polarization Characteristics.



Oxidant, 70% HNO_3 . Porous Teflon, 19μ , 0.025 in. thick

Figure 11. Diffusion Rate of HNO_3 Vapor Through Porous Teflon.

The data obtained at 30°C seem to represent only variations in liquid diffusion through pinholes, since very little vapor diffusion should occur with an HNO₃ vapor pressure of only 2-3 mm. It is fairly certain that the data at 90°C represent mostly vapor diffusion, since even the highest leakage rate at 30°C could not account for the high diffusion rate of the untreated sample at 90°C. (Liquid diffusion is proportional to the square of the absolute temperature.)

It should be pointed out that the 19-μ pore size Teflon sheet used for diffusion tests does not have the same thickness as that used in the 19-μ pore size electrodes used for electrochemical tests in Section B-2-b. This accounts for the difference in current density of the two testing methods. It was felt that less liquid leakage could be encountered with the thicker Teflon sheet, resulting in more accurate vapor diffusion comparisons for the thicker material.

(4) Conclusions

All of the data seem to point to the carbon-Teflon bond as being the limiting feature of this type of construction. The factors entering into the control of this bond are numerous; time, temperature, and bonding pressure along with the state of the Teflon and carbon surfaces are critical for deforming and plugging electrode pores. A careful investigation of these variables might lead to a method of providing usable, reproducible diffusion rates, although such a study would be a long and exacting undertaking. Before starting such a line of investigation, a second approach to making Teflon vapor diffusion electrodes is being evaluated.

3. Teflon Diffusion Electrodes from Teflon Powder Bonded to Solid Carbon

a. Background

Changes in diffusion rates through porous Teflon sheet that are caused by the bonding led to the use of a porous carbon matrix as the diffusion control barrier. If a homogeneous wet-proof surface layer of pores can be formed by melting Teflon powder into the surface of porous carbon, a network of very thin controlled diffusion paths should occur. The diffusion rate can be controlled by the amount of Teflon powder applied per unit area of the porous carbon.

b. Experimental

An initial preparation of Teflon powder-carbon electrodes was made using Teflon powder on FC-14 porous carbon. About 6 mg/cm² of Teflon powder was pressed between two 1/16-in. thick rectangles of FC-14 carbon.

(1) Current-Voltage Relations

The electrode was tested using 70% HNO_3 in the diffusion compartment and 5M H_2SO_4 electrolyte at 90°C . As soon as 70% HNO_3 was added, the electrode was cathodically polarized until a constant potential of 1.0 v vs SHE was attained, corresponding to a current density of 210 ma/cm². Product gas (NO) emerged from both sides of the carbon electrode. Qualitatively, more gas was discharged from the diffusion compartment than from the electrolyte side.

(2) Longer-Term Testing

The electrode described above was operated overnight at 120 ma/cm². The lower current density allowed lower diffusion rate as the HNO_3 was consumed. The relation of vapor pressure of HNO_3 to HNO_3 concentration and temperature is shown in Figure 12. The voltage-current relationship for a 26-hour test is shown in Figure 13. The electrode would not perform as well when a fresh HNO_3 charge was used.

(3) Contamination

After 2 hours and 20 hours, samples of the electrolyte were tested for contamination and found to contain 0.01M and 0.03M HNO_3 , respectively.

c. Discussion

This initial test shows the possibility of obtaining high diffusion rates with low contamination levels with the Teflon diffusion electrode structure. The ease of construction makes it preferable to the porous Teflon sheet construction. However, before deciding on only one type of Teflon electrode construction two important qualifications for electrode candidates should be determined:

- (1) Electrode life -- wetproofing as well as polarization characteristics.
- (2) Reproducibility.

C. ANODE DEVELOPMENT

1. Catalytic Activity of Precious Metals for the Anodic Oxidation of N_2H_4 in H_3PO_4

a. Background

At this time, Pt is the only known catalyst that is selective to the anodic oxidation of N_2H_4 in the presence of any reasonable concentration of HNO_3 . Since we know that Pt is not the best catalyst

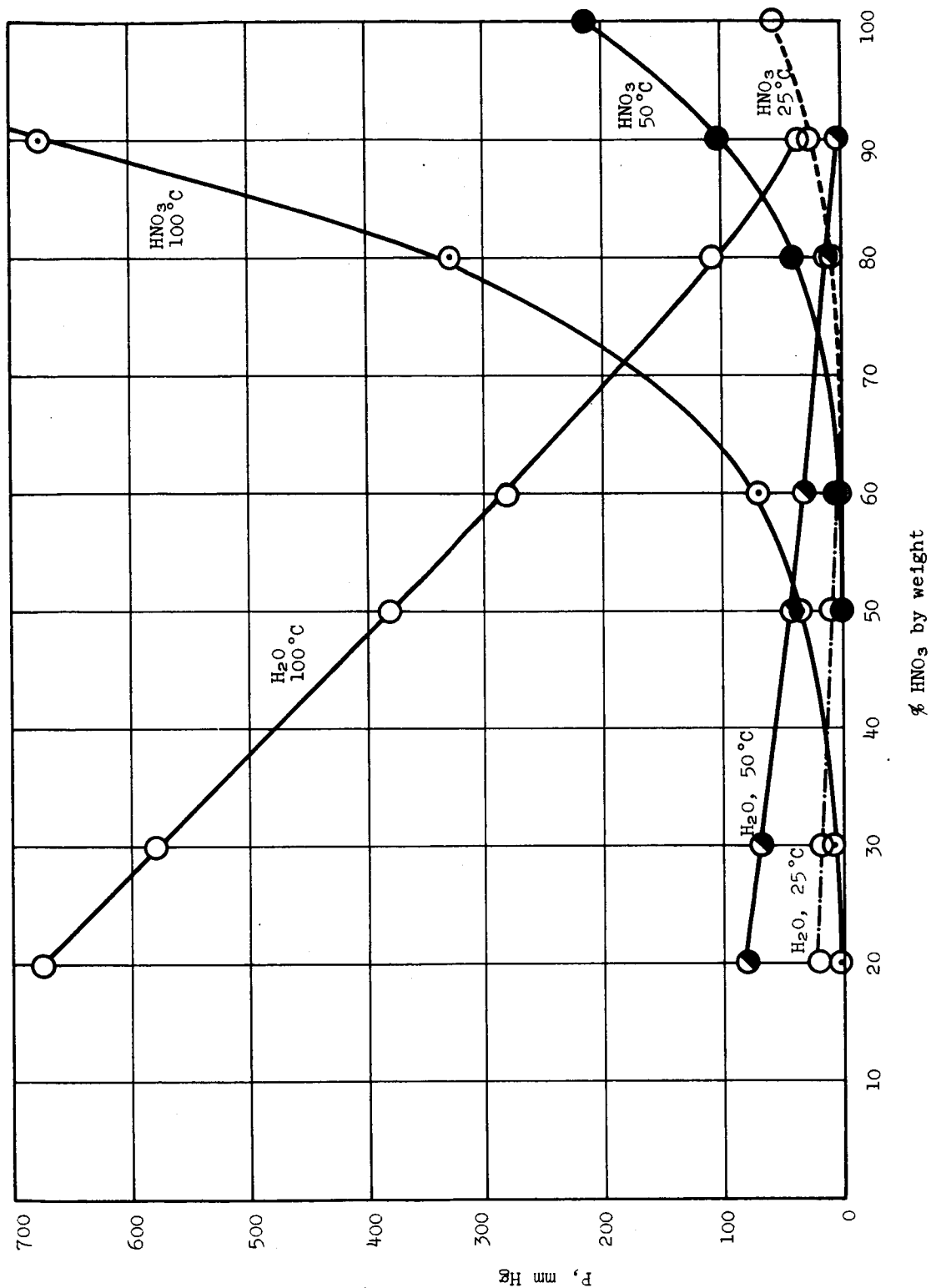
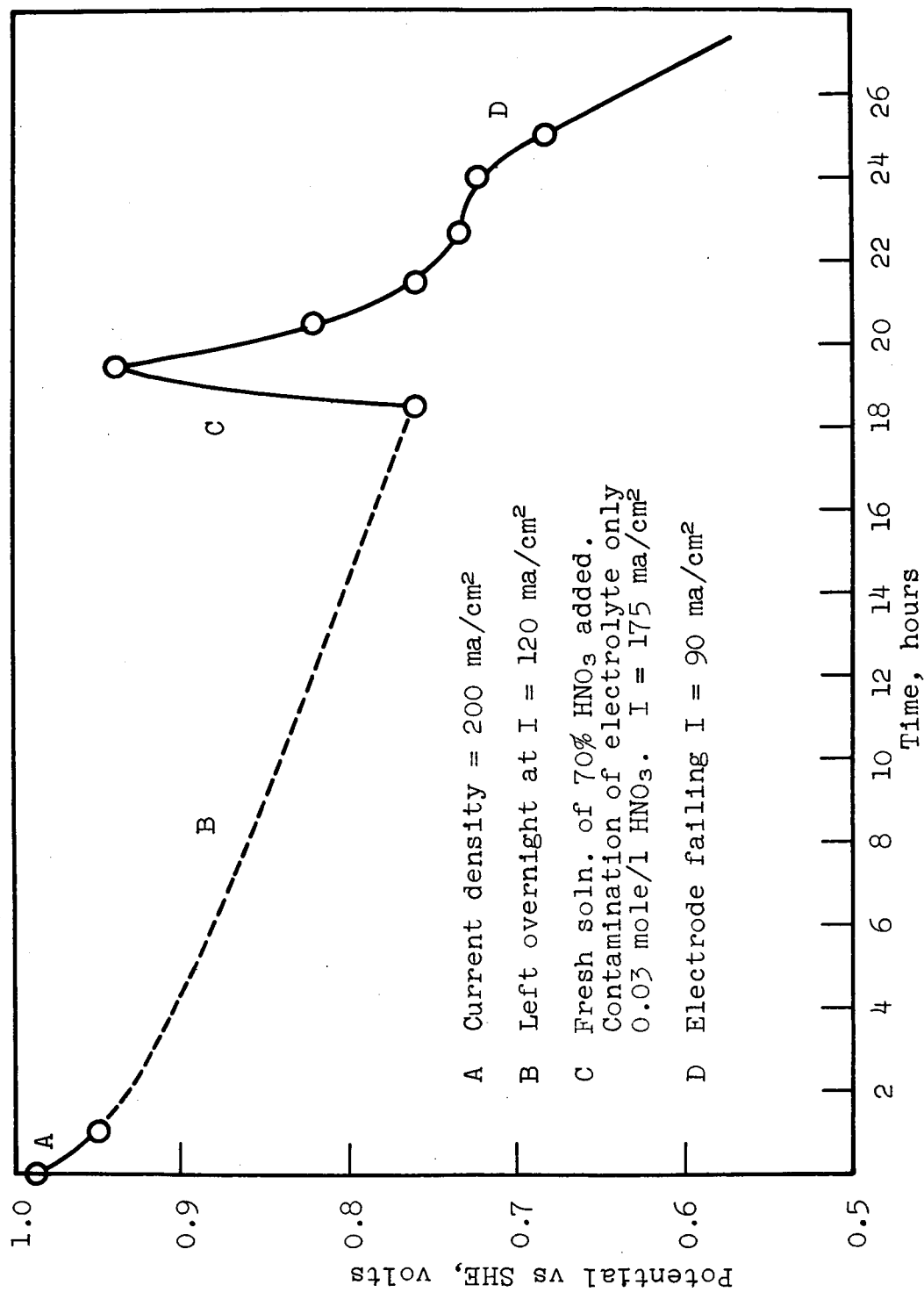


Figure 12. Variation of Vapor Pressure of HNO₃-H₂O Mixtures at 25, 50 and 100°C.
Data from "Systematic Inorganic Chemistry", D. M. Yost and H. Russell, Jr.
Pentice-Hall, Inc., 1946.



6 mg/cm² Teflon Powder
 Heat impregnated into
 FC-14 carbon electrode.

Electrolyte 5M H₂SO₄
 Temp. 90°C

Figure 13. Long-Term Cathodic Polarization of HNO₃ Teflon Diffusion Cathode.

for N_2H_4 oxidation in H_3PO_4 solution when no HNO_3 is present, a search for other catalytic materials was initiated.

b. Non-Contaminated Solutions

Polarization tests for catalytic activity on carbon electrode surfaces are given in Table 1. Both chemiplated and electroplated precious metals were used when possible. One sample of pure Pt black powder* in a tantalum holder Teflon electrode construction was used (Run 5, Table 1). The following trends were noted as a result of tests in uncontaminated solutions:

- (1) Tests 2-4, Table 1, indicate that amount of platinum per unit area is the controlling factor in electrode activity, regardless of type of deposit.
- (2) The activity of all chemiplated mixtures is superior to any of the chemiplated metals alone at equal loadings. The best of the mixtures is 60% Pt-20% Ru-20% Au, which has an advantage over any chemiplated pure component at 100 ma/cm².
- (3) Electroplated Rh at very low loading is superior to electroplated Pt at significantly higher loadings and is the best catalyst other than the commercial Pt black electrode listed in Table 1.

c. Contaminated Solutions Containing 1M HNO_3

Only the electroplated Rh and most Pt-containing electrodes showed significant selectivity toward N_2H_4 oxidation in H_3PO_4 solutions containing 1M HNO_3 . The Rh electrode (test no. 6, Table 1) had less than 0.1 v deterioration of potential in the contaminated solution, as compared with the potential in the uncontaminated solution.

2. Diffusion-Controlled Anodes

a. Background

The development of diffusion-controlled anodes using Teflon as a waterproofing agent is needed for concurrent use with the cathode diffusion electrode in full-cell application. The primary goal of our anode study is this development. However, before a detailed investigation is started, the catalyst must be selected. Tentatively, Pt is being tested with diffusion-controlled systems.

b. Results

Only constructions utilizing the tantalum holder with porous Teflon sheet molded to the catalyst powder have been made and tested as

* Engelhard Industries, Inc., Newark, N. J.

Table 1

ANODIC POLARIZATION OF PRECIOUS METAL CATALYSTS FOR N_2H_4 ANODES

Fuel: $0.5M N_2H_4$
 Electrolyte: $5M H_3PO_4$
 (Both Uncontaminated and
 Contaminated with $1M HNO_3$)
 Temperature: $90^\circ C$

Catalyst	Type Deposit #	mg/cm ²	wt %	Anode Potential (Volts vs SHE)##						Plating Solution	
				Current Density (ma/cm ²)		Current Density (ma/cm ²)		Current Density (ma/cm ²)			
				OCV	50	100	OCV	50	100		OCV
1. FC-13 Carbon (control)	-	-	-	0.54	-	-	0.59	-	-	-	
2. Platinum	P	13.5	8.2	0.20	0.37	0.49	0.31	0.46	0.58	3% H ₂ PtCl ₆	
3. Platinum	P	12.5	7.7	0.14	0.43	0.53	0.33	0.46	0.56	0.3% Pb (Ac) ₂	
4. Platinum	C	4.9	3.3	0.19	0.50	0.60	0.27	0.57	0.79	*	
5. Platinum	B	25	-	0.14	0.22	0.25	0.34	0.38	0.40	**	
6. Rhodium	P	6.7	4.3	0.14	0.27	0.35	0.30	0.34	0.43	1% RhCl ₃	
7. Rhodium	C	3.7	1.7	0.23	0.48	0.59	0.40	-	-	*	
8. Ruthenium	P	25	14.5	0.19	0.29	0.40	0.39	0.55	0.64	1% RuCl ₃	
9. Ruthenium	C	7.9	5.3	0.19	0.38	0.59	0.38	-	-	*	
10. Palladium	P	17.3	9.0	0.26	0.45	0.52	0.54	-	-	1% PdCl ₂	
11. Gold	C	2.8	1.9	0.41	0.55	0.64	0.46	0.64	-	*	
12. 80%Pt-20%Ru	C	2.9	2.0	0.17	0.335	0.45	0.34	0.55	-	*	
13. 67%IR-33%Ru	C	11.4	7.6	0.19	0.40	0.55	0.36	-	-	*	
14. Iridium	C	2.6	1.8	0.27	0.51	0.61	0.40	0.62	-	*	
15. 60%Pt-20%Ru-20%Au	C	4.0	2.7	0.16	0.30	0.44	0.32	0.54	0.62	*	

* Reduced with $NaBH_4$ ** Tantalum diffusion electrode construction
(see Section B-1-a)

IR-Free

P - Electroplated on FC-13 Carbon
(Pure Carbon Company)

C - Chemiplated on FC-13 Carbon

B - Commercial Metallic Black on Pt
Screen Grid

diffusion-controlled anodes. The same problems found in cathode electrode construction were prevalent for the anode, and diffusion control of a concentrated N_2H_4 source has not been obtained.

Methods of using commercial blacks as well as plated and chemi-plated coatings in diffusion anodes are now being developed. One path of investigation is to follow the development of the carbon black-powdered Teflon cathode construction with a Pt catalyst added.

D. CONCLUSIONS (POROUS TEFLON VAPOR DIFFUSION ELECTRODES -- ANODE AND CATHODE)

Vapor diffusion type cathode construction has reached the stage of full-cell testing. The following electrode requirements have been met:

- (1) The electrodes deteriorate a maximum of 0.14 v in up to 0.5M N_2H_4 in 5M H_3PO_4 (see Figure 5).
- (2) The electrolyte is only slightly contaminated by leakage of unreacted HNO_3 through the cathode (see Figure 13).
- (3) The electrode can control limiting current densities from 50 to 200 ma/cm² at 1.0 v vs SHE (see page 20 and Figure 13).
- (4) Dual construction electrodes can be used for half-cell testing.
- (5) Diffusion electrodes have a life of at least 24 hours at 90°C (see Figure 13).
- (6) Platinum, as an anode catalyst in soluble fuel systems in H_3PO_4 electrolyte can tolerate at least 1M HNO_3 , which is above the expected contamination level from the HNO_3 cathode. Rhodium, along with some chemiplated mixtures, might prove to be superior at contamination levels expected in full cell use (see Table I, Conclusion 2).
- (7) Diffusion-controlled full cells utilizing concentrated fuel and oxidant feeds have at least short-term feasibility in a compatible acid electrolyte system using the reactants N_2H_4 and HNO_3 .
- (8) Dinitrogen tetroxide, N_2O_4 , would be expected to be readily substituted for the HNO_3 oxidant with the same electrode structure (see Figure 2).

E. FUTURE PLANS (ELECTRODE DEVELOPMENT PROGRAM)

1. Cathodes

- (1) Test for reproducibility with impregnated Teflon powder construction for the dual carbon electrode.

- (2) Determine the loadings of Teflon powder required for different limiting current densities.
- (3) Determine the range of currents and potentials that can be attained without gross contamination of the electrolyte with specific electrodes developed under (2).
- (4) Determine the long-term characteristics of the above electrodes.

2. Anodes

- (1) Test commercial metallic blacks for catalytic activity for the anodic oxidation of N_2H_4 on non-carbon substrates with and without contamination.
- (2) Develop diffusion electrodes for the anodic oxidation of N_2H_4 , using the best selective catalyst either on carbon or metal substrate.
- (3) Determine the life of the diffusion electrodes.

3. Full Cells

Integrate suitable anodes and cathodes into small scale cell units for testing.

III. FULL CELLS WITH ION EXCHANGE MEMBRANES

A. BACKGROUND

1. Organic Ion Exchange Membranes

The use of ion exchange membranes (IEM) as so-called "solid electrolytes" is of considerable interest in this program because of the IEM's theoretical ability to isolate noncompatible fuel-oxidizer combinations.

Solid palladium membrane hydrogen diffusion electrodes are not currently available with resistance to the corrosive action of HNO_3 oxidant. Therefore, the possibility of using a palladium membrane anode in conjunction with a HNO_3 cathode depends on physical separation of anolyte and catholyte. An ion exchange membrane electrolyte with suitable properties could effect this physical separation.

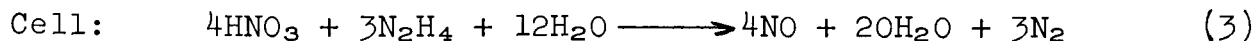
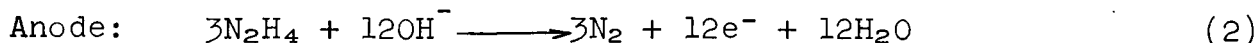
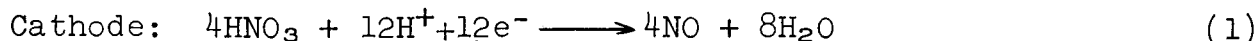
Additionally, the extremely high voltages and low polarization afforded by the acid-base cell (HNO_3 catholyte-separator- N_2H_4 in 5-10M KOH) make this construction of considerable interest. Again, an ion exchange membrane provides the most convenient route to such a construction.

The principal properties required of an IEM for this duty are:

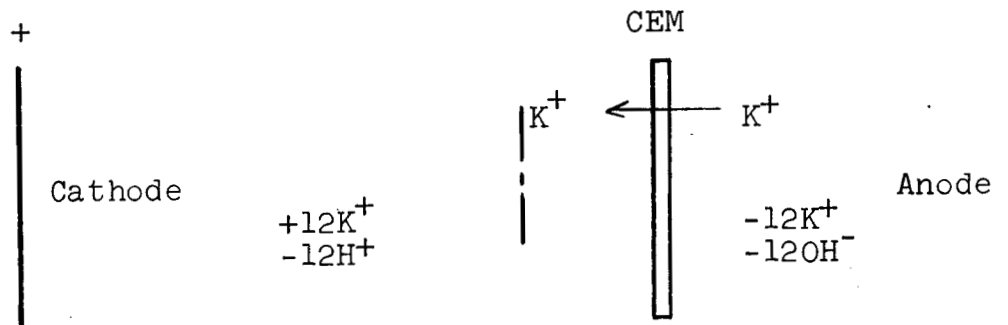
1. Long-term resistance to HNO_3 , and strong base,
2. Low internal electrical resistance,
3. Good mechanical strength, and
4. Moderate heat resistance.

Previous work in this laboratory (ref. 3) indicated that some available anion and cation exchange membranes possessed these properties to a limited extent.

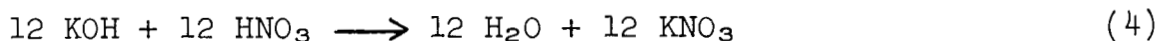
The operation of the HNO_3 - N_2H_4 cell with an IEM involves transfer of potassium ions from the KOH fuel carrier through the membrane and into the cathode compartment in addition to the cathodic reduction of HNO_3 and the anodic oxidation of N_2H_4 . The cell reactions are summarized as follows:



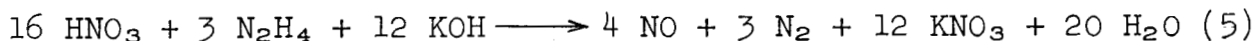
To transfer 12 Faradays of current across the cation exchange membrane (CEM), 12 potassium equivalents must migrate from the anolyte through the cation membrane and into the catholyte:



The generation of 12 Faradays of current by reaction (3) by the membrane cell will then require the gain of 12 K^+ and the loss of 12 H^+ in the catholyte and the loss of 12 K^+ and 12 OH^- in the anolyte. This is equivalent to the overall neutralization reaction:



Adding equation (4) to equation (3) gives an equation for the complete oxidation, reduction, and neutralization reactions required for cell operation:



$$\Delta F^\circ = -494 \text{ Kcal/g-mole}; E^\circ = 1.78 \text{ v}$$

2. Zirconium Phosphate Separators

Organic ion exchange membranes have limited life in concentrated acids, bases, or oxidizing agents (ref. 4). Inorganic ion exchangers incorporated in an inert binding fabric may be more durable than organic membranes in contact with corrosive reactants such as HNO_3 . Zirconium phosphate has been studied as a cation exchanger (refs. 5,6, and 7), and several methods of preparing the compound have been described (ref. 5,6,8).

Zirconium phosphate crystals exhibit cation exchange properties and are reported to be stable in strong acid (13M HNO_3) and also in base up to a pH of at least 13 (ref. 5).

B. METHOD

1. Cell Description

Full cell evaluation of cation exchange membranes was conducted using an adaptation of the 3 x 3 in. cell construction described in Quarterly Report No. 1.

All membranes were obtained from commercial sources. Ion exchange membranes were cut to 5 x 5 in. dimensions and punched to accommodate the end plate bolts. Each membrane served as its own gasket to seal the cell.

The palladized nickel anode was selected because of its high activity and relative economy. Furthermore, failure of the IEM would be readily apparent from appearance of nickel nitrate byproduct resulting from HNO_3 attack on the anode.

In all cases, the fuel/potassium hydroxide (KOH) mixture was pumped through the anode cavity at a rate of approximately 200 cc/min.

Cell temperature was maintained by heating the fuel/base mixture in the fuel tank, with anolyte recirculation providing adequate heat transfer to the cell. Nitric acid was circulated either by pumping or by a gas lift energized by byproduct NO . Concentration of the HNO_3 stream was allowed to decrease from 15M to a minimum of 5M, at which point the entire oxidizer charge was replaced.

Because both anode and cathode characteristics were well defined, complete polarization data on each cell were not taken. Runs were made at the maximum current density consistent with voltage stability. Load for the cell was provided either by a resistor or dc power supply.

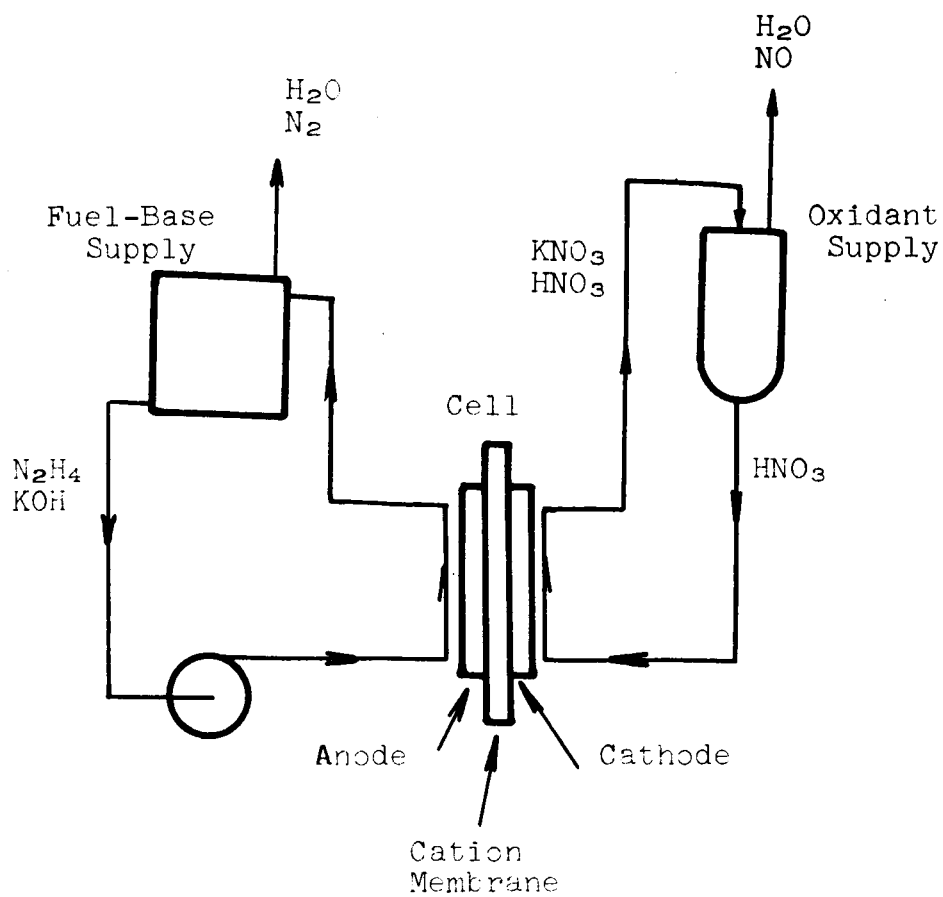
The full cell reactant handling system is shown schematically in Figure 14, for the case where oxidant is circulated by gas lift.

2. Zirconium Phosphate Separators

Zirconium phosphate was prepared by mixing either zirconium sulfate or zirconyl chloride with H_3PO_4 . The washed precipitate was pressed between two sheets of Teflon felt at 800 psig, 220°F, for 1 hour. A flexible, integral cation exchange separator resulted. This separator was incorporated into Cell 61507, listed in Table 2.

C. RESULTS AND DISCUSSION

Table 2 summarizes construction and operation of the types of ion exchange membrane cells studied during this quarter.



N_2H_4 / KOH - Cation Exchange Membrane - HNO_3
 Electrode Dimensions - 3 by 3 in.

Figure 14. Fuel Cell and Pumping System

Table 2
SUMMARY OF ION EXCHANGE MEMBRANE FULL CELLS

Electrode Area: 9 in.²

Cell No.	Anode	Cathode	Membrane	Fuel	Oxidant	Performance Summary	Notes
54905	1.0 mil thick Pd foil Rhodium plated, heated to 650°C	Platinized 100-mesh 5 mil Platinum screen supported on 22 mil thick 304SS expanded metal.	Ionics, Inc., 61A22-183 cation exchange membrane	8% N ₂ H ₄ ·H ₂ O	5M HNO ₃	OCV = 1.0 volt at 70 ma/cm ² Life = 10 min Temperature = 30°C Ecell = 0.8 volt	Acid penetrated pinholes in IEM and attacked Pd anode.
54906	25 mil thick Goulds nickel plaque, 20 mg/in. ² Pd catalyst	Duplicate of 54905	Duplicate of 54905	1M N ₂ H ₄ in 5M KOH (pumped)	10M HNO ₃ (circulated by gas lift)	See Figure 15. Life = 8 hours Run at 120 ma/cm ² , 1.55 v. Temperature = 60°C	IEM badly attacked by HNO ₃ . Numerous holes in membrane.
54918	Duplicate of 54906	Duplicate of 54905	Duplicate of 54905 Membrane from fresh supply	1M N ₂ H ₄ in 5M KOH (pumped)	15M HNO ₃ (pumped)	OCV = 2.1 volts Run at 120 ma/cm ² , 1.4 v Temperature = 70°C Life = 9 hours	Failure same as 54906
61508	Duplicate of 54906	Duplicate of 54905	Duplicate of 54918 10 mil thick woven glass cloth between cathode and membrane	1M N ₂ H ₄ in 5M KOH (pumped)	15M HNO ₃ (circulated by gas lift)	OCV = 2.2 volts Run at 100 ma/cm ² , 1.1 v for 8 hours Temperature = 70°C Life = 8 hours	Glass cloth deteriorated exposing IEM to direct HNO ₃ attack.
54911	Duplicate of 54906	Duplicate of 54905	Duplicate of 54918 15 mil thick asbestos between cathode and membrane.	1M N ₂ H ₄ in 5M KOH (pumped)	15M HNO ₃ (pumped)	OCV = 1.9 volts Run at 70 ma/cm ² , 1.0 v Temperature = 70°C Life = 32 hours	Fragile asbestos paper finally ripped, exposing IEM to HNO ₃ attack.
54916	Duplicate of 54906	Duplicate of 54905	Duplicate of 54918 25 mil thick Teflon felt between cathode and IEM	1M N ₂ H ₄ in 5M KOH (pumped)	15M HNO ₃ (circulated by gas lift for first 58 hours; pumped to end)	OCV = 1.9 volts Run at 70 ma/cm ² , 1.1 v Temperature = 70°C Life = 70 hours	IEM showed attack and pinhole leaks in area of acid inlet and outlet manifolds, indicating deleterious effect of rapid pumping.

Table 2 (continued)
SUMMARY OF ION EXCHANGE MEMBRANE FULL CELLS

Cell No.	Anode	Cathode	Membrane	Fuel	Oxidant	Performance Summary	Notes
61509	Duplicate of 54906	Duplicate of 54905	AMF cation exchange membrane C-313	1M NaH_4 in 5M KOH (pumped)	15M HNO_3 (pumped)	OCV = 2.1 volts Run at 50 ma/cm ² , 1.5 v Temperature = 70°C Life = 2-1/2 hours	Cell gradually fell off to negligible output. IEM very brittle from action of caustic.
61510	Duplicate of 54906	Duplicate of 54905	Duplicate of 61509 25 mil thick Teflon felt between cathode and IEM	1M NaH_4 in 5M KOH (pumped)	15M HNO_3 (pumped)	Performance same as 61509. Life = 3 hours	No change in performance with time-developed serious leak in Teflon felt seal which required shutdown. IEM again showed caustic embrittlement.
61512	Duplicate of 54906	Duplicate of 54905	Permion 1010†† cation exchange membrane	1M NaH_4 in 5M KOH (pumped)	15M HNO_3 (pumped)	OCV = 2.2 volts Immediate deterioration No life	Anolyte stream showed immediate HNO_3 attack on nickel anode. IEM was sample and apparently contained pinhole leaks.
61507	Duplicate of 54906	Duplicate of 54905	Monsanto Research zirconium phosphate separator	1M NaH_4 in 5M KOH (pumped)	15M HNO_3 (pumped)	OCV = 2.1 volts Run at 70 ma/cm ² , 0.94 v Temperature = 70°C Life = 3 hours	Failed due to HNO_3 attack on anode. Zirconium phosphate deteriorated by caustic and washed out of separator, permitting mixing of acid and base.

* Ionics, Inc., Cambridge, Massachusetts.

** Gould National Batteries, St. Paul, Minnesota.

† Johns-Manville Corp., Fuel Cell Paper, Tilton, New Hampshire.

†† Radiation Applications Company, Long Island, New York.

‡ TE2050 - American Felt Company, Glenville, Connecticut.

1. N_2H_4 | Pd(Rh) | CEM | Pt | HNO_3 (Cell 54905)

The rapid deterioration of the palladium membrane anode by HNO_3 attack indicates the need for an IEM completely impervious to acid back leakage. This leakage occurred with relatively dilute HNO_3 catholyte (5M).

Despite the failure, the good initial open circuit voltage (OCV) and total polarization of only 0.2 volt from actual OCV at 70 ma/cm² and 30°C are indicative of reasonable performance to be expected from suitably protected palladium membrane anodes.

2. N_2H_4 (in KOH) | Ni(Pd) | CEM | Pt | HNO_3 (Cell 54906 and 54918)

This cell is characteristic of the performance of the Ionics 61AZ2-183 cation exchange membrane. Figure 15 illustrates the degree of polarization and power density with increasing current density. Electrical performance is adequate, but the membrane's poor resistance to HNO_3 limits the effective life of the cell to 7-12 hours.

The fresh membrane material used in Cell 54918 performed similarly to the older material used in Cell 54906.

3. Porous Fiber Mat

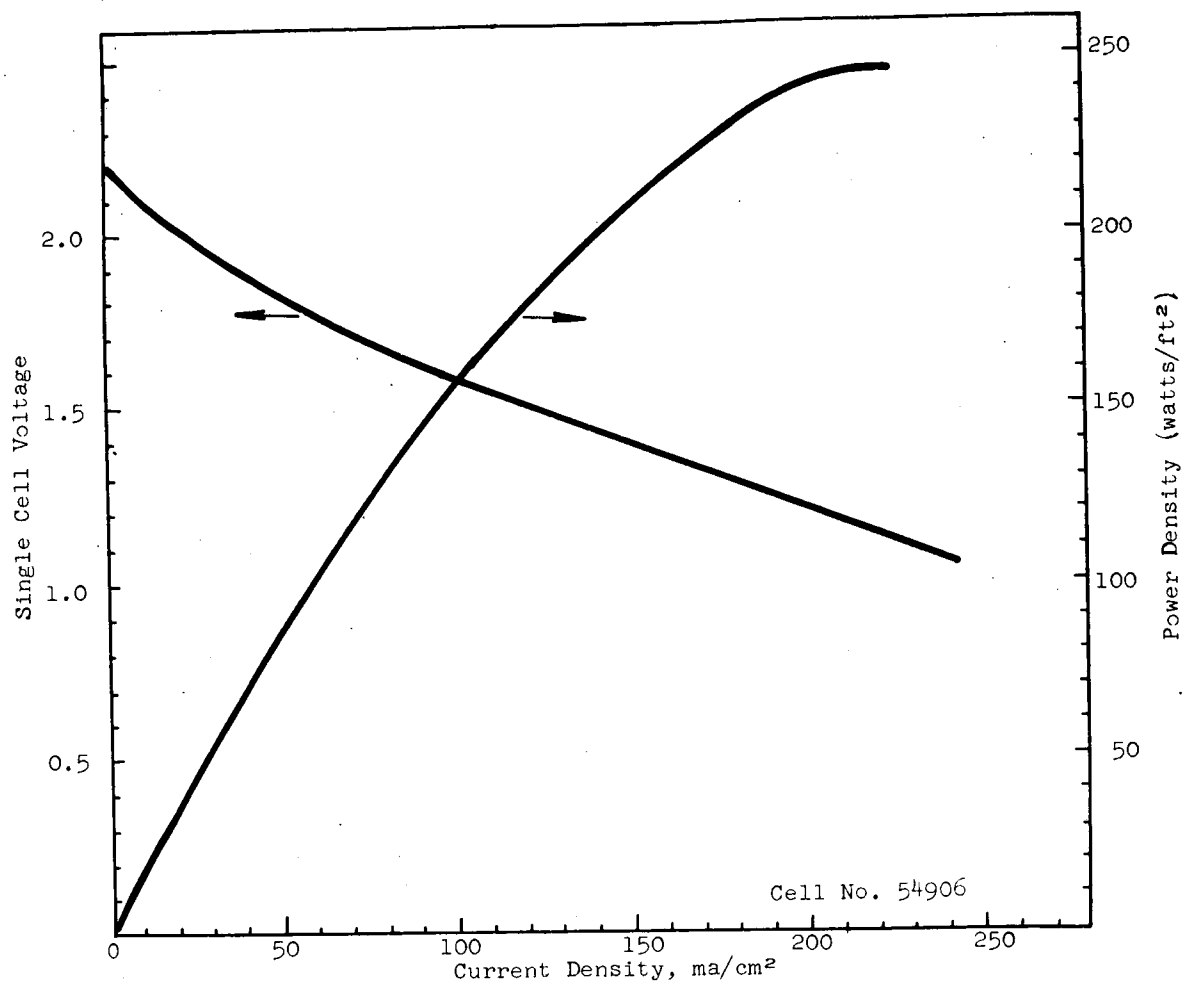
To protect the cation exchange membrane from direct contact with HNO_3 , a series of cells was constructed incorporating a porous fiber mat between the cathode and IEM. Hopefully, potassium ions migrating through the membrane would react with NO_3^- ions to form a layer of KNO_3 , which would be retained in the porous mat material. This salt layer would effectively limit access of HNO_3 to the IEM surface. A decrease in electrical performance was expected because of the increased IR drop resulting from the extra distance between electrodes and the higher resistance of the KNO_3 solution.

4. N_2H_4 (in KOH) | Ni(Pd) | CEM | Glass Fiber | Pt | HNO_3 (Cell 61508)

This cell employed a layer of woven glass cloth as the porous mat. At 100 ma/cm² a decrease in voltage performance of about 30% was noted. Life was only 8 hours. Dissassembly of the cell showed that the glass cloth was torn in several places and had lost its flexibility. Apparently binders used in the cloth had been attacked by the strong acid, causing failure to structural integrity and rapid attack on the exposed IEM.

5. N_2H_4 (in KOH) | Ni(Pd) | CEM | Asbestos Mat | Pt | HNO_3 (cell 54911)

Cell 54911 incorporated a 15 mil thick asbestos paper as the porous layer. Voltage performance at 70 ma/cm² was about 40% poorer than that of Cell 54906, but an effective life of 32 hours was obtained. Inspection of the failed cell components showed that the fragile asbestos sheet had torn, probably as a result of high catholyte liquid velocities.



1M N_2H_4 / 5M KOH - Cation Exchange Membrane - 10M HNO_3
 Operating Temperature: 60°C
 Electrode Area: 9 in²

Figure 15. Voltage and Power Density Characteristics of N_2H_4 - HNO_3 Fuel Cell with Cation Exchange Membrane

6. N₂H₄ (in KOH) | Ni(Pd) | CEM | Teflon Felt | Pt | HNO₃

Cell 54916 was operated at 70 ma/cm², 1.1 volt, and 70°C for 70 hours before IEM failure. Protective buffer material between cathode and IEM was 25 mil thick Teflon felt. The failed membrane showed appreciable HNO₃ attack only in the catholyte manifold areas, suggesting again that rapid pumping of acid tends to wash out the protective KNO₃ layer where liquid velocities are highest. This could be modified with design changes.

7. N₂H₄ (in KOH) | Ni(Pd) | CEM | Pt | HNO₃ (Cell 61509)

Cell 61509 and 61510 tested a commercial cation exchange membrane (AMF-C-313) from another source. Electrical performance was only moderate, the cell being unable to stably carry current densities higher than about 50 ma/cm². Cell 61509 probably leaked HNO₃ slowly through the IEM to gradually polarize the anode and ultimately attack it.

8. N₂H₄ (in KOH) | Ni(Pd) | CEM | Teflon Felt | Pt | HNO₃ (Cell 61510)

Cell 61510 used the Teflon felt buffer with the AMF-C-313 membrane. Electrical performance was approximately the same as that of Cell 61509, the increased internal resistance caused by the Teflon felt probably being nearly equivalent to Cell 61509's poisoned anode effect. Difficulty in sealing the cell forced a shut down after 3 hours when HNO₃ leakage out of the cell became excessive. There was no fall-off in electrical output with time.

The AMF C-313 membrane showed good resistance to HNO₃ but became quite brittle when exposed to the strongly basic anolyte stream. Testing was therefore discontinued with this membrane in the acid/base cell, though it could have application in a nitric acid/hydrazine (in pH 6-12 solution) cell.

9. N₂H₄ (in KOH) | Ni(Pd) | CEM | Pt | HNO₃ (Cell 61512)

The Permion 1010 cation exchange membrane was also evaluated. This is a very thin membrane and the small sample available either contained pinhole leaks when supplied or was punctured during cell assembly. No performance data were obtained because of immediate leakage of HNO₃ to the anode compartment. A new sample is on order and suitable precautions will be taken to insure its undamaged installation in a cell.

10. N₂H₄ (in KOH) | Ni(Pd) | CEM | Zr Phosphate | Pt | HNO₃ (Cell 61507)

The zirconium phosphate separator was incorporated into Cell 61507. An OCV of 2.1 volts was obtained, and the cell was run at 70 ma/cm² and 0.94 volt at 70°C before gradual decrease in electrical performance. After 3 hours, leakage of HNO₃ to the anode was observed and the cell was shut down. Examination showed deterioration of the zirconium

phosphate layer in the separator probably by basic attack. This material should have better application in cells with hydrazine in pH 6-12 solution.

Other zirconium phosphate separators were prepared by forming the precipitate in asbestos sheet or loose fibers. Subsequent processing included washing out of excess acid, drying, shredding, and pressing into sheet form. The resulting separators although integral, were judged too fragile for fuel cell use.

D. CONCLUSIONS

The acid/base fuel cell possesses attractive electrical output performance if a suitable ion-exchange membrane can be found to provide effective solution separation over a long period of time.

The life of commercial IEM's presently available can be extended from about 8 hours to at least 70 hours for the $\text{HNO}_3/\text{N}_2\text{H}_4$ -in-base system. This improvement in life is obtained by employing a buffer layer of porous material between the cathode and IEM. The porous layer apparently becomes loaded with neutralization products that shield the IEM from direct acid attack. This is considered new technology.

Of the several commercial IEM's tested for $\text{HNO}_3/\text{N}_2\text{H}_4$ -in-base fuel cell systems, none exhibit completely satisfactory qualities. Further tests are needed to characterize the Permion 1010 membrane.

Zirconium phosphate ion exchange separators for fuel cell use have been fabricated and tested. Results are still inconclusive but specialized applications appear likely. The method of fabrication and the form of zirconium phosphate separators are considered new technology.

E. FUTURE PROGRAMS

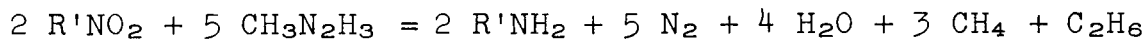
- (1) Retest Permion 1010 membrane
- (2) Test other membranes as they are obtained.
- (3) Make limited investigation of zirconium phosphate separators.
- (4) Evaluate cells with HNO_3 cathode, N_2H_4 in pH 6-12 solution anodes.

IV. MONOMETHYL HYDRAZINE REFORMING

A. BACKGROUND

The desirability of monomethyl hydrazine (MMH) as a rocket fuel has been well defined in previous reports (ref. 9). Since no efficient MMH fuel cell anode has been found, it is desirable to first decompose MMH to hydrogen, nitrogen, and carbon dioxide.

Kuhn (ref. 10) has described the catalytic reduction of organic nitro compounds with MMH. Using a 5% palladium-charcoal catalyst, products contained nitrogen, methane, and ethane; the reaction evidently was:



Liquid phase decomposition of hydrazine to nitrogen and hydrogen has been reported by Tanatar (ref. 11) using platinum black as catalyst. Under the correct conditions it seems likely that MMH will undergo a similar decomposition.

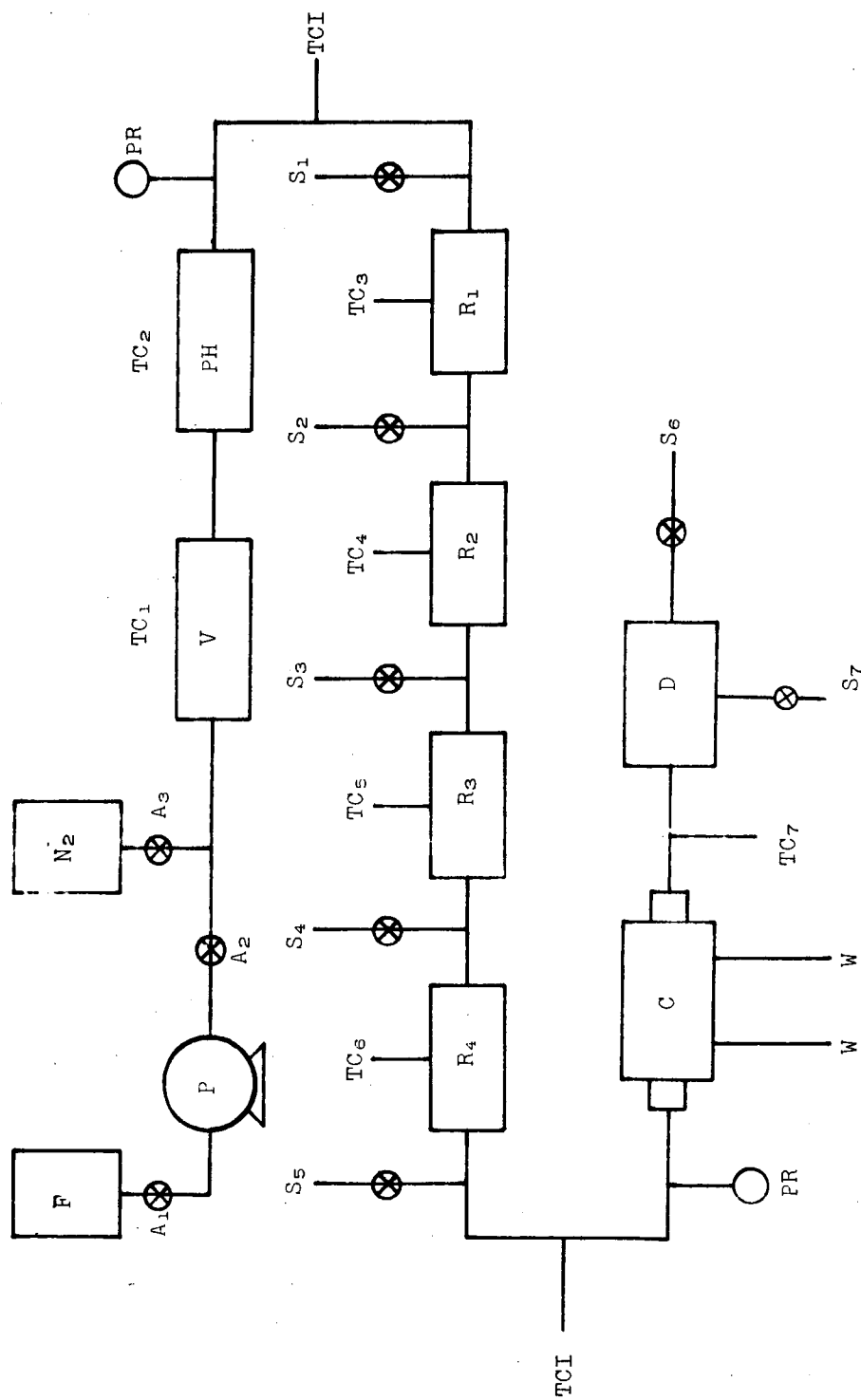
The complete decomposition of MMH to nitrogen, hydrogen, and carbon dioxide will require either converting any methane formed to CO_2 or inhibiting the formation of the methane in preference to CO_2 .

B. METHOD

Construction was started of a catalytic reformer as shown schematically in Figure 16. The system consists of a feedtank, pump, vaporizer, preheater, four identical reacting sections, a condenser, and a separator. When the unit is in operation, MMH and water will be fed as liquids.

The reactor sections are 6-in. lengths of 304 stainless steel tubing, 5/8 in. O.D. with 0.065 in. walls. The use of tube fittings enables the easy replacement of a section without removal of all four reacting sections. Also, mixed catalyst combinations and preliminary screening tests can be made easily. Sampling lines preceding and following the reactor sections enable an evaluation of each catalyst tested in a given run.

Heat is supplied by electrical heating tape wrapped around the vaporizer, preheater, and catalyst sections. Thermocouples on all the heated sections plus two in-stream thermocouples will facilitate close control of temperature throughout the system. Cooling water will be used to condense the product stream, leaving CO_2 , N_2 , H_2 , and any other product gases for analysis by gas chromatography. Pressure gages and relief valves are also incorporated in the system.



F = Feed tank
 P = Pump
 N₂ = Nitrogen cylinder
 V = Vaporizer
 PH = Preheater
 C = Condenser
 D = Separator
 A = Feed valves
 W = Cooling water
 PR = Pressure gage and relief
 TCI = In-stream thermocouple
 S = Sample line
 TC = Thermocouple
 R = Reacting section

Legend

Figure 16. Catalytic Reformer

C. FUTURE PROGRAM (MONOMETHYL HYDRAZINE REFORMING)

- (1) Complete the reformer system. (The system is about 75% completed.)
- (2) Operate the reformer.
- (3) Evaluate catalysts such as Pd, Pt, Ni, and others in combinations and on different supports such as carbon, alumina, and silica.

V. PALLADIUM-HYDROGEN DIFFUSION ELECTRODE

A. BACKGROUND

The solid Pd hydrogen diffusion electrode is attractive for fuel cell systems using hydrogen gas or materials that can be converted to hydrogen. The Pd membrane not only provides an electrically conducting electrode but also can absorb and transfer hydrogen (and only hydrogen) from the fuel side of the electrode to the electrolyte side for use as an anode fuel. Other materials cannot penetrate the electrode, so soluble fuels such as hydrazine can be restricted from the electrolyte compartment where they could diffuse to and degrade the cathode. A detailed discussion of the background of the Pd diffusion electrode was given in the last quarter's report (ref. 18).

The activation of Pd diffusion electrodes by oxidation was described in the last quarter. Activation was further increased by plating with Rh black before the oxidation. The catalytic action produced by oxidation was also attributed to the thin oxide film, which is a p-type semiconductor (cation vacancy type). Heat treating foils in a hydrogen atmosphere degraded the electrodes by reducing the Pd oxide catalytic film.

During the second quarter, the effect of alloying elements with Pd-25%Ag electrodes and oxides of these elements on the performance of the diffusion electrode were studied. Metallographic examination and electron micro-probe analyses on the cross sections of these foils were made to determine the structure of the electrodes, particularly of the diffusion layer. The Pd-Pt-Ag alloy was studied as a HNO_3 -resistant H_2 diffusion anode. The effect of SO_2 in the oxidizing atmosphere during Pd heat treatment was studied. Studies of the effect of plating Rh on the Pd-25%Ag diffusion electrode were continued. The substitution of PdO by the more stable rhodium oxide as a catalyst was attempted. Life tests of a number of diffusion electrodes with various treatments were made.

B. EFFECT OF ALLOYING ELEMENTS

1. Constitution of Alloys

Elements selected for alloying with palladium foil were classified into the following categories:

a. Valencies of the most stable metal ions.

High valency metals	- Fe, Ir, Ru, Th, Ti, Zr
Low valency metals	- Ag, Cu, Li
Bivalency metals	- Co, Mg, Ni, Pt
Alloys	- Zr-Ni, Ni-Cr

(b) Types of oxides formed by these metals.

n-Type semiconductor - $\text{Fe}(\text{Fe}_2\text{O}_3)$, $\text{Mg}(\text{MgO})$, $\text{Th}(\text{ThO}_2)$,
 $\text{Ti}(\text{TiO}_2)$, $\text{Zr}(\text{ZrO}_2)$

p-Type semiconductor - $\text{Ag}(\text{Ag}_2\text{O})$, $\text{Co}(\text{CoO})$, $\text{Cu}(\text{Cu}_2\text{O})$,
 $\text{Fe}(\text{FeO})$, $\text{Ni}(\text{NiO})$

Amphoteric type semi-
conductors - $\text{Ir}(\text{IrO}_2)$, $\text{Ru}(\text{RuO}_2)$, $\text{Ti}(\text{TiO}$, $\text{Ti}_2\text{O}_3)$

(c) Thermal characteristics of hydrogen occlusion

Exothermic - Th , Ti , Zr (Ir , Rh)*

Endothermic - Ag , Co , Cu , Fe , Ni , Pt

Brief descriptions of the binary phase diagrams (ref. 12) of the above elements with palladium are given in the Appendix.

2. Preparation of Alloy Foils

Since we are primarily interested in the surface composition of the Pd-25% Ag foil, alloying elements were diffused into the surface after application of the alloying metal by electroplating, vacuum evaporation, or compound decomposition techniques. Details of the methods used to prepare and heat treat alloys with Pd-25% Ag foils are given in the Appendix. Three electrodes were prepared for each alloying element. One electrode was plated on both surfaces, and the other two were plated on only one side.

3. Anodic Polarization Characteristics

Polarization data have been determined by the procedure and with the cell described in the first quarter's report (ref. 18). Hydrogen gas was the fuel and 5M KOH the electrolyte.

a. Plating on Both Sides of the Electrode

Current density-potential data for electrodes alloyed on both sides determined potentiostatically at 25, 60, and 90°C are given in Table 3. Elements in Table 3 are arranged as follows:

(1) From No. 1 to No. 3: The foil was alloyed almost uniformly across the thickness.

(2) No. 4 and 5: Not uniform alloying across the thickness, but sufficiently deep diffusion layer and considerable amount of alloying element near the surface of the foil.

* Uncertain about thermal characteristics and practically are not hydrogen occluders

Table 3

ANODIC CURRENT DENSITIES, ma/cm^2 , FOR Pd-25%Ag ELECTRODES
WITH DIFFUSED ALLOYING ELEMENTS

Electrode: 0.001-in. Pd-25%Ag foil diffused with
an alloying element on both sides.
Electrolyte: 5M KOH
Fuel: H_2 gas

Metal	Temp °C	OCP* v	Overpotential (η) vs HE**				
			0.1	0.2	0.3	0.4	0.5
Fe	25	0.09	0.1	0.25	0.6	1.3	2.6
	60	0.03	0.25	0.95	2.4	4.6	8.8
	90	0.03	0.4	1.3	3.2	5.8	10.0
Cu	25	0.74	None				
	60	0.74	None				
	90	0.68	None				
Ag	25	0.24	-	≈ 0.3	0.8	1.7	2.5
	60	0.13	-	4.5	6.2	7.4	8.2
	90	0.16	-	8.0	11.0	13.0	14.5
Co	25	0.00	1.1	9.5	27.5	52	72
	60	0.00	1.5	8.0	23.0	40	58
	90	0.00	6.6	19.0	26.0	51	70
Ni	25	0.06	<1.0	<1.0	1.5	4.0	9.0
	60	0.09	-	0.9	2.6	6.8	15.0
	90	0.04	-	2.0	6.5	14.0	32.0
Ru (a)	25	0.06	-	0.8	1.6	3.1	5.0
	60	0.04	-	1.3	2.6	4.0	5.6
	90	0.12	0.8	1.3	2.3	3.6	5.5
Ru (b)	25	0.00	0.4	1.8	5.6	10.0	16.5
Rh	25	0.00	10	24	40	63	100
	60	0.00	22	52	90	140	225
	90	0.00	40	100	180	330	(400 at $\eta=0.43\text{v}$)
Ir	25	0.00	18	50	93	145	200
	60	0.03	13	40	80	120	170
	90	0.03	20	50	93	130	200

Table 3 (continued)

ANODIC CURRENT DENSITIES, ma/cm^2 , FOR Pd-25%Ag ELECTRODES
WITH DIFFUSED ALLOYING ELEMENTS

Metal	Temp °C	OCP* v	Overpotential (η) vs HE**				
			0.1	0.2	0.3	0.4	0.5
Pt	25	0.00	42	96	170	210	250
	60	0.00	90	160	270	340	370
	90	0.00	140	370	(400 at $\eta=0.23\text{v}$)		
Mg	25	0.00	1.4	5.0	9.8	15.0	21.5
	60	0.00	0.8	1.6	-	-	-
	90	-	-	-	-	-	-
Ti	25	0.01	4	14	42	82	155
	60	0.01	7	22	49	102	205
	90	0.02	15	52	100	195	350
Zr	25	0.02	0.45	4.8	8.4	13.5	26
	60	0.00	2.7	16.5	21.0	26.5	46
	90	0.02	11.2	26.5	28.5	40	90
Th	25	0.00	1.5	7.6	23	61	140
	60	0.00	1.8	12.5	44	78	170
	90	0.00	8.2	43	88	135	250
Zr-Ni	25	0.05	1.65	5.1	15	45	120
	60	0.02	2.9	14	42	120	235
	90	0.02	8	31	60	120	270
Ni-Cr (80-20)	25	0.03	-	0.12	0.28	0.55	1.1
	60	0.03	0.13	0.54	1.18	1.6	2.4
	90	0.03	0.52	1.7	3.1	3.7	5.1
None	25	0.02	1.3	3.2	8.0	16.0	40.0
	60	0.02	1.0	4.0	9.4	19.0	49.0
	90	0.02	3.8	14.5	23.5	44.0	115.0

* Open Circuit Potential vs HE.

** Hydrogen electrode potential in the same electrolyte
and at the same temperature.

(3) From No. 6 to No. 9: Large amounts of the alloying element were deposited, but a deep diffusion layer was not formed.

(4) From No. 10 to No. 13: Smaller amounts of alloying element were deposited by vacuum evaporation.

(5) No. 14 and 15: Alloy deposition by vacuum evaporation.

Within each group above, the elements were arranged according to the periodicity of elements.

b. Plating on One Side of the Electrode

Anode current density of the foils plated on one side at the overpotential of 0.5 v vs HE are given in Table 4.

During the determination of polarization characteristics, a kind of oversaturation was observed on some electrodes, particularly on those that showed good performance at room temperature. Such electrodes carried very high current densities at elevated temperatures, and, as the current density was further increased, the current dropped significantly and then increased as the polarization increased. The oversaturation was perhaps due to a slow recovery of a severe concentration gradient of H_2 caused by high current polarization at lower temperature. Before attaining equilibrium with H_2 at the higher temperature, the electrode could carry higher current densities than those under the equilibrium. This phenomenon was more noticeable for electrodes that were plated on their fuel sides. A typical curve for an electrode that was plated with Rh on the fuel side is shown in Figure 17. One of the electrodes showing oversaturation was immediately polarized downward (from high to low current) after the upward polarization curve was recorded. The continuous downward curve is shown as curve D in Figure 17.

4. Discussion and Conclusions

Our original plan for this study was to alloy Pd-25% Ag with metals that could be plated on the surface of the foil and heated to promote alloy formation by diffusion. These electrodes would then be used to determine the effect of alloying with a third component upon the polarization characteristics of the electrode when used as a H_2 anode. Some elements, such as Ag, Cu, Fe, Co, and Ni, diffused rapidly enough into the Pd-25% Ag foil to form a definite alloy layer, although some of the unalloyed element was left on the surface of the electrodes. Such elements as Pt, Ru, and Rh, however, diffused so slowly that a comparatively thin diffusion layer was formed on the foil, and the majority of the elements remained on the foil surface. A considerable amount of Pd actually diffused into the deposited layer. Other groups of elements, Mg, Ti, Zr, and Th, were deposited in small quantities

Table 4

EFFECT OF ALLOYING ON ONE SIDE OF THE
Pd-25% Ag DIFFUSION ELECTRODE

(Anodic current densities ma/cm² at 0.5 volt vs HE)

Electrode: 0.001-in. Pd-25% Ag foil alloyed
 Electrolyte: 5M KOH
 Fuel: H₂ gas
 Temp: 25°C

<u>Metal</u>	<u>Plating</u>	
	<u>Fuel Side</u>	<u>Electrolyte Side</u>
None	40.0	40.0
Fe	11.0	65.0
Cu	2.6	0.1
Ag	3.9	3.3
Co	140.0	8.0
Ni	110.0	34.0
Ru	110.0	44.0
Rh	25.0	>400.0
Ir	180.0	240.0
Pt	210.0	38.0
Mg	110.0	66.0
Ti	80.0	125.0
Zr	36.0	43.0
Th	115.0	155.0
Ni-Zr	27.0	170.0
Ni-Cr	17.0	3.3

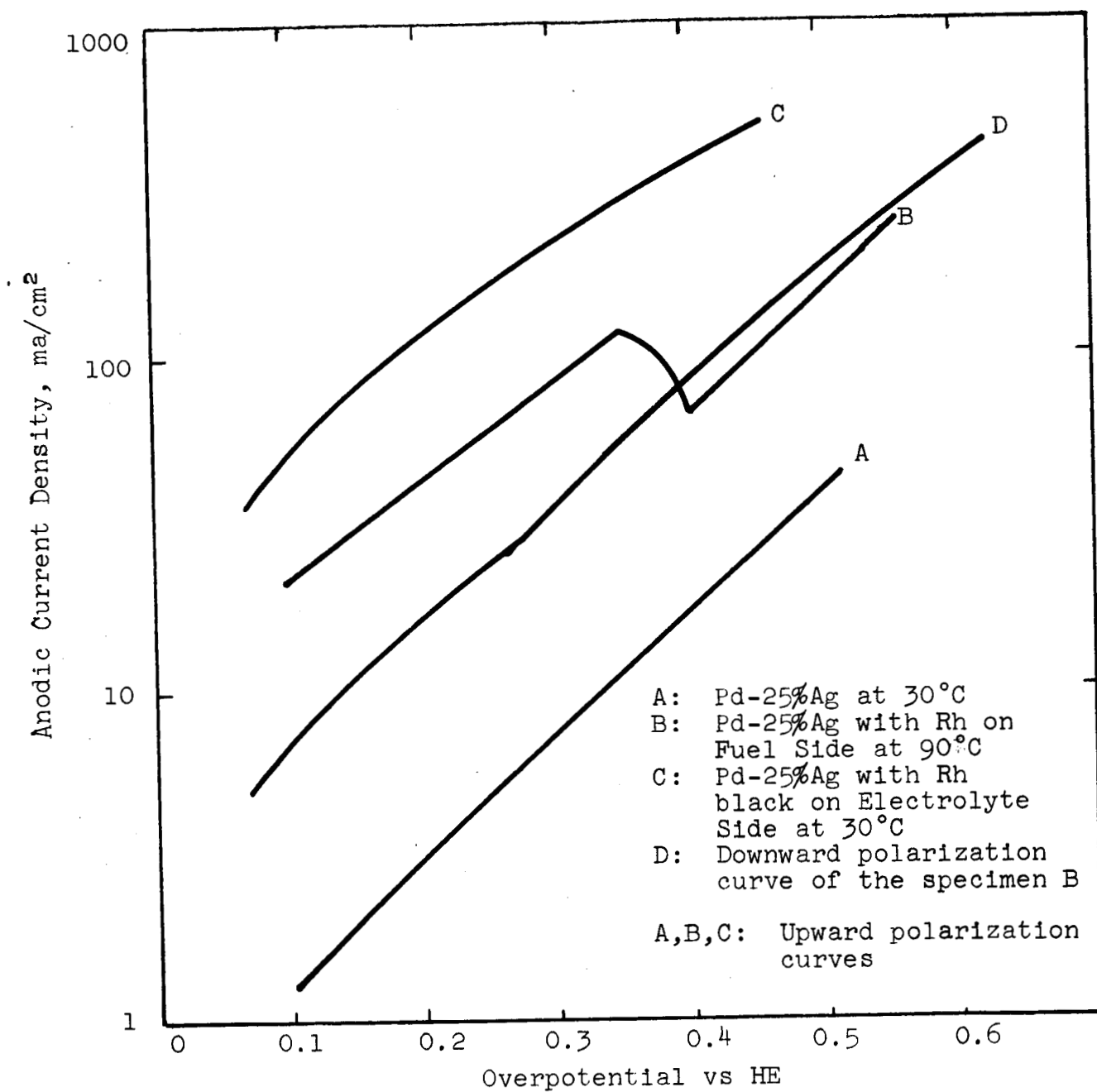


Figure 17. Effect of Alloying Pd-25%Ag Electrode With Rh on Anodic Polarization

on the surface of the foil but, since these elements were O₂ getters, they were oxidized by traces of O₂ in argon before sufficient diffusion occurred. With the above considerations in mind, certain general conclusions regarding the effect of added elements on polarization behavior of the Pd-25% Ag system can be made:

(1) Alloying with low valency metals (Ag and Cu) is unfavorable to anodic polarization characteristics.

(2) Improvement of polarization characteristics is obtained by alloying with high valency metals (Ir, Rh, Ru, Pt, Ti, and Rh).

(3) Alloying of exothermic hydrogen occluders improved the electrode performance.

(4) An increase in temperature decreased polarization.

(5) The effect of alloying on the fuel side is independent of the effect on the electrolyte side.

(6) Alloying on the fuel side of the electrode does not significantly change the slope of the straight portion of the polarization curve of the Pd-25% Ag foil with no plating, and curves are approximately parallel. Alloying on the electrolyte side changed both slope and height of the polarization curves of Pd-25% Ag electrode, as shown in Figure 17.

(7) Some of the best elements to improve the anodic polarization of the Pd-25% Ag diffusion electrode were:

Fuel side:	Pt, Ir, and Co
Electrolyte side:	Rh, Ir, and Ni-Zr
Both sides together:	Pt, Rh, and Ir

C. EFFECT OF MIXED OXIDES ON SURFACE CATALYSIS

1. Background

The original plan for Pd-25% Ag electrode catalytic treatment was to test the effect on electrode performance of adding a third metal to the PdO layer, according to the concepts that cation vacancy sites in the PdO layer act catalytically, and a change of concentration of vacancies caused by the presence of a foreign metal should affect the electrode performance. However, since the amount of PdO is so small, it is almost impossible to control the amount of added element to the PdO surface. Consequently, an improved technique would be to plate much more of the added metal than the final amount of PdO surface coating. The plated surface would then be heated to form mixed oxides of Pd and the added metal, without appreciable diffusion of the metal into the Pd-25% Ag foil.

2. Electrode Preparation

Pd-25% Ag foil was annealed in an argon atmosphere for two hours at 850°C and then oxidized in air for two hours at 700°C. A third metal was then deposited, either by electroplating or by vacuum deposition. Finally, the foil was again oxidized in air for two hours at 700°C. It was hoped that the last temperature for the final oxidation was not high enough to allow substantial diffusion of the deposited metal into the foil, since the PdO layer could act as a diffusion barrier.

The exact condition of the surface was determined by metallographic and microprobe analyses. The amount of metal deposited was approximately 0.1 mg/cm² by electroplating and 0.01 mg/cm² by vacuum evaporation.

3. Polarization Characteristics

Table 5 gives anodic polarization characteristics of the electrodes plated on both sides with third metals and oxidized, together with data on a control electrode with no plating. Elements in Table 5 were arranged according to their chemical periodicity. Elements that belong to the same periodic group were arranged according to their molecular weights.

Table 6 gives anodic polarization characteristics of the electrodes plated either on the fuel side or on the electrolyte side alone in terms of current density at an overpotential 0.5 v vs HE at 30°C.

During this series of tests, the oversaturation phenomenon discussed in the previous section was observed on anodic polarization curves of almost all electrodes except the electrodes coated with Mg. The phenomenon was particularly significant on the electrodes coated on the fuel side.

4. Discussion and Conclusions

Data for the effect of mixed oxides as surface catalysts were more consistent than those for the alloyed electrodes. The reason is perhaps that approximately the same amount of metal was on the electrode surface regardless of whether metals were oxidized or not, since no diffusion took place during the heat treatment. However, the surface concentration of these metal oxides varied because of different rates of oxidation of some metals. Those elements that were electroplated might be present in too great concentrations on the surfaces, since it is believed that a catalyst coating should be very thin. An excess of oxide inhibits good polarization characteristics because of poor electrical conductance and possibly slow diffusion of H₂ through the oxide layer.

Table 5

ANODIC CURRENT DENSITIES, ma/cm², FOR Pd-25%Ag ELECTRODES
COATED WITH OTHER METAL OXIDES

Electrode: 0.001-in. Pd-25%Ag foil with
another metal oxide on both sides.
Electrolyte: 5M KOH
Fuel: H₂ gas

Metal	Temp °C	OCP* v	Overpotential (η) vs HE**				
			0.1	0.2	0.3	0.4	0.5
Li	25	0.64	none	-	-	-	-
	60	0.03	3.1	11.5	30	54	57
	90	0.01	10.0	29.0	60	60	60
Mg	30	0.00	1.9	6.0	12.0	19.5	28
	60	0.00	3.3	11.2	17.0	27.0	37
	90	0.00	5.7	14.5	24.5	37.5	48
Ti	30	0.00	0.9	5.7	18.5	32	57
	60	0.00	10	32	36.5	34	56
	90	0.00	34	82	68	60	42
Zr	30	0.03	0.46	2.8	9.3	25	58
	60	0.03	4	10	16	18.5	60
	90	0.03	13	32.5	34	47	105
Th	30	0.00	0.9	5.6	16	29	50
	60	0.00	2.0	5.0	11.0	18.0	40
	90	0.00	2.4	7.6	13.5	18.5	29
Co	30	0.06	2.0	18.5	37	62	83
	60	0.06	1.7	10.5	30	48	67
	90	0.06	3.3	24	38	62	86
Ni	30	0.00	4.2	17	54	210	(400 at $\eta=0.45v$)
	60	0.00	8.4	40	160	(400 at $\eta=0.38v$)	
	90	0.03	17	82	260	(400 at $\eta=0.33v$)	
Ru	30	0.00	11.5	38	94	195	380
	60	0.00	16.5	60	125	280	(400 at $\eta=0.46v$)
	90	0.00	42	155	390	(400 at $\eta=0.31v$)	

Table 5 (continued)

ANODIC CURRENT DENSITIES, ma/cm^2 , FOR Pd-25%Ag ELECTRODES
COATED WITH OTHER METAL OXIDES

Metal	Temp °C	OCP* v	Overpotential (η) vs HE**				
			0.1	0.2	0.3	0.4	0.5
Rh	30	0.00	38	83	155	210	300
	60	0.00	74	130	195	260	360
	90	0.00			(400 at $\eta=0.08$ v)		
Pt	30	0.02	22	68	200	(400 at $\eta=0.37$ v)	
	60	0.03	26	100	300	(400 at $\eta=0.37$ v)	
	90	0.03	43	140	310	(400 at $\eta=0.33$ v)	
Cu	30	0.24	-	-	2.3	4.3	10.5
	60	0.11	-	-	3.7	9.0	18.5
	90	0.17	0.9	2.6	7.8	12.5	19.0
Zr-Ni	30	0.00	1.3	7.7	24	56	100
	60	0.00	2.0	10	28	64	115
	90	0.03	11	40	83	130	220
Ni-Cr	30	0.06	0.13	0.63	1.8	3.8	8.0
	60	0.06	0.9	2.4	4.0	5.5	10.0
	90	0.06	7.6	15.5	11.0	12.0	22.5
None	25	0.02	1.3	3.2	8.0	16.0	40.0
	30	0.02	0.5	2.8	8.4	19.0	42.0
	60	0.02	1.1	4.0	9.4	19.0	49.0
	90	0.02	3.8	14.5	23.5	44.0	115.0

* Open Circuit Potential

** Hydrogen electrode potential in the same solution
and at the same temperature.

Table 6

EFFECT OF FOREIGN METAL OXIDE ON ONE SIDE
OF PD-25%Ag DIFFUSION ELECTRODE
(Anodic Current Densities ma/cm² at 0.5 Volts vs HE)

Electrode: 0.001-in. Pd-25%Ag foil covered with
foreign metal oxide (or mixed with PdO)

Electrolyte: 5M KOH

Fuel: H₂ gas

Temperature: Room temperature (25°C)

<u>Plating</u>	<u>Li</u>	<u>Mg</u>	<u>Ti</u>	<u>Zr</u>	<u>Th</u>	<u>Co</u>	<u>Ni</u>	<u>Ru</u>	<u>Rh</u>	<u>Pt</u>	<u>Cu</u>	<u>Zr-Ni</u>	<u>Ni-Cr</u>
Fuel side	93	120	40	48	220	35	70	115	95	82	120	60	20
Electrolyte side	120	100	175	10	92	110	>400	140	>400	>400	6.8	13	3.2

Because of various amounts of oxides of the individual metals, the true mechanism of the catalytic activity of these metal oxides is not clearly understood. However, there are some indications of correlation of the catalytic activity with the fundamental nature of the elements, that is, the "periodicity" of the elements, as shown in Figure 18.

The following empirical observations of general effects of mixed oxides on electrode performance were made after examining the data in Tables 5 and 6, although there are a small number of exceptions.

- (1) Elements that strongly activate the electrolyte side are the best catalysts when plated on both sides of the electrode, although they were not the best activators on the fuel side (Ni, Pt, Rh, and Ru).
- (2) Oxides of the p-type semiconductors were better activators than those of n-type semiconductors when the metals were plated on both sides of the electrode or on the electrolyte side only.

p-type semiconductor group: Ni, Co, Pt, Rh, and Ru (Amphoteric RuO_2 could act as a cation vacancy type oxide)

n-type semiconductor group: Mg, Zr, Ti, Th, and Cr.

- (3) Some n-type semiconductor oxides improved the anodic polarization of Pd-25%Ag electrodes when they were plated on one side of the electrode, only one particular side (Ti on electrolyte side) or even both sides individually (Mg and Th). However, when the electrodes were plated with these metals on both sides, negative or no effects resulted.
- (4) Thermal characteristics of hydrogen occlusion have no effects, since metals plated did not diffuse into the foil and stayed on the surface either as the oxides or as a powdery deposit.
- (5) Valency of elements might affect polarization characteristics to some extent, but the effects must be minor.
- (6) Some of the best oxides to improve the anodic polarization of Pd-25% Ag diffusion electrodes were:

Fuel side: Th, Cu, Ru, and Mg
Electrolyte side: Ni, Pt, and Rh
Both sides together: Pt, Rh, Ru, and Ni

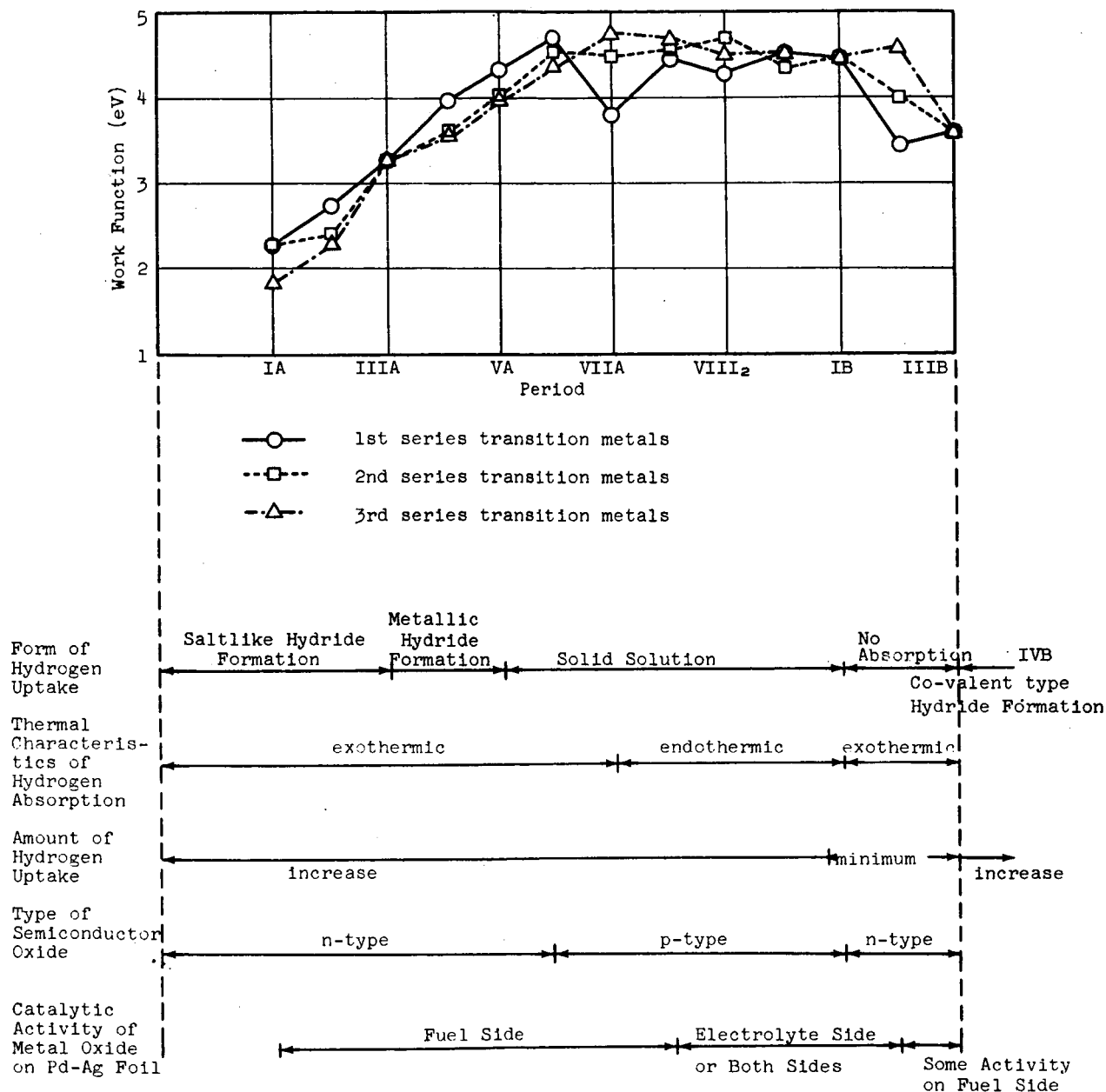


Figure 18. Some Periodic Characteristics of Transition Metal Elements Related with Hydrogen Diffusion Electrode

D. METALLOGRAPHIC STUDIES AND DETERMINATION OF THICKNESS OF THE DIFFUSION LAYER

Metallographic examinations and electron microprobe analyses were made on cross sections of Pd-25% Ag electrodes that were plated on either one side or both sides with other elements.

One set of foils was diffusion treated in argon for 2 hours at 850°C before oxidation treatment in air for 2 hours at 700°C. The other set of foils was annealed at 850°C and then oxidized in air for 2 hours at 700°C before plating, and again oxidized in air for 2 hours at 700°C after plating. Metallographic examination and electron microprobe analyses were made after those foils were tested for anodic polarization.

1. Metallography

Metallographic examinations showed a drastic change of structure on those electrodes that were plated and diffused with rapid diffusing elements such as Fe, Cu, and Co. These materials showed finely divided intermetallic crystal structures. The foil plated and diffused with Ni also showed a significant change. On the other hand, the foils plated and diffused with slow diffusing elements showed almost the same structure as that of Pd-25% Ag. Plated silver diffused into the foil rapidly but did not significantly change the structure, since palladium and silver form a continuous series of solid solutions. The foils plated by vacuum evaporation also showed no visible change on the structure.

The foils plated and oxidized without diffusion treatment did not change the structure of the foil, indicating that metals and alloys plated were oxidized without significant diffusion.

The foil plated and diffused with rhodium showed numerous microcracks across the foil. Typical metallographic photographs are shown in Figures 19 to 24.

2. Electron Microprobe Analyses*

Microprobe examination of Pd-25% Ag foils that were plated and diffused with other metals indicated that the rates of diffusion were extremely different from one element to another, resulting in various thicknesses in the diffusion layers. Diffusion rates for Cu, Co, and Fe were very fast, resulting in uniform alloying of approximately 10% of the foil thickness. A small amount of excess Cu, Co, and Fe remained on the surface, which is believed to be oxidized during the heat treatment. The thickness of the diffusion layer of Pd into the excess metal layer was about 2μ ($1\mu = 10^{-4}$ cm) for Cu, 1μ for Co, and about 0.5μ for Fe.

*Electron microprobe analyzer Model JXA-3A, Japan Electron Optics Lab, Co., Tokyo, Japan



Figure 19. Pd-25%Ag Foil Plated on Both Sides with Rh, Diffused in Argon and Oxidized in Air. After Electrochemical Tests. x500

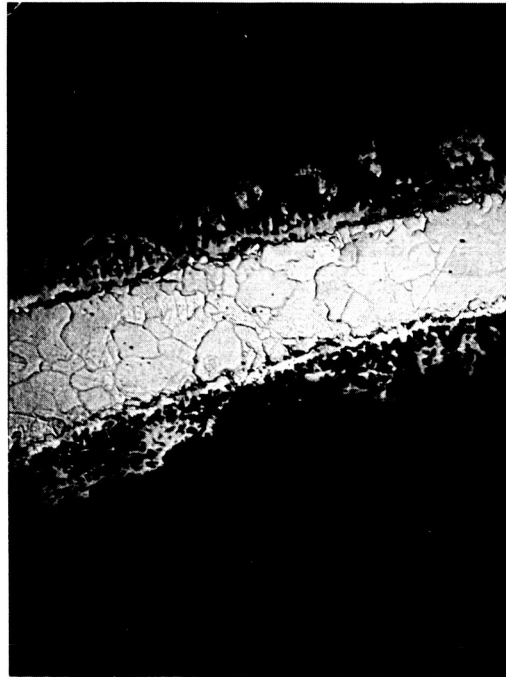


Figure 20. Pd-25%Ag Foil Plated on Both Sides with Pt, Diffused in Argon and Oxidized in Air. After Electrochemical Tests. x500

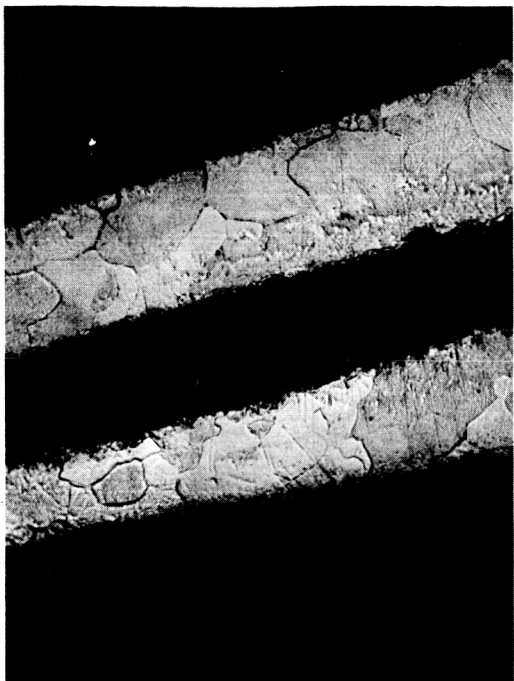


Figure 21. Pd-25%Ag Foil Plated on Both Sides with Ni, Diffused in Argon and Oxidized in Air. After Electrochemical Tests. x500

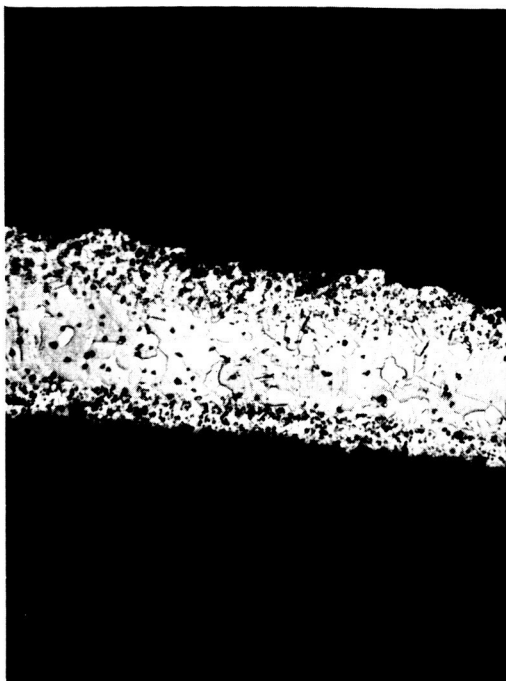


Figure 22. Pd-25%Ag Foil Plated on Both Sides with Cu, Diffused in Argon and Oxidized in Air. After Electrochemical Tests. x500



Figure 23. Pd-25%Ag Foil Plated on Both Sides with Ag, Diffused in Argon and Oxidized in Air. After Electrochemical Tests. x500

Etchant for all specimens:

Mixture of 5% KCN and 5% $(\text{NH}_4)_2\text{SO}_4$ with trace of KI crystals at room temperature.

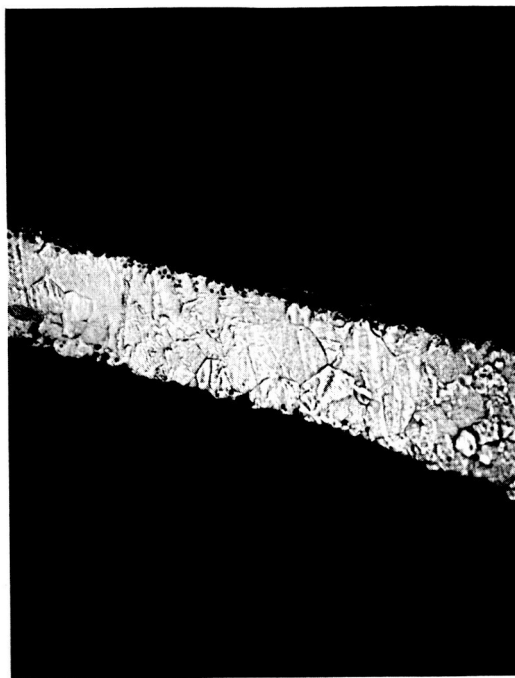


Figure 24. Pd-25%Ag Foil Coated on Both Sides with Ir by IrCl_3 Decomposition, Diffused in Argon and Oxidized in Air. After Electrochemical Tests. x500

Diffusion of Ni was somewhat slower than that of Cu, Fe, or Pd. The thickness of the diffusion layer was about 10μ , and the highest concentration of Ni in the foil was about 5%, resulting in a considerable amount of unalloyed Ni on the electrode surface. The thickness of the diffusion layer of Pd into the excess Ni layer was about 1μ .

Diffusion of Rh, Pt, or Ir was much slower than that of Cu, Fe, or Ni, but the diffusion of Pd into Rh, Pt, or Ir was much faster; every particle of powdery deposits of Rh, Pt, or Ir contained a significant amount of Pd. The thickness of the diffusion layer at the surface of the foil was approximately 8μ , 6μ , and 2μ , respectively, for Pt, Rh, and Ir. Among these three elements, only Rh showed some indication of further diffusion into the bulk of the foil. However, the concentration of Rh in the bulk was so small that data were not conclusive by the method used.

Almost no diffusion was observed on Ru, Ti, and Zr.

Foils plated and diffused on only one side with Ag, Cu, Fe, and Co showed that these elements diffused so rapidly that even the unplated side contained some of these elements diffused from the other side during the treatment. Foils plated and diffused with other elements on one side showed that alloying was limited to the plated side.

Foils plated and oxidized without the diffusion process showed no diffusion on those elements that are readily oxidized. However, elements that cannot be readily oxidized, such as Pt, diffused to some extent into the foil, and some Pd diffused into the plated layer. Diffusion of Pd into the plated layer took place to a small extent also in the case of Ni Plate. Typical curves of the analyses to document these observations are shown in the Appendix.

E. PLATINUM-PALLADIUM-SILVER ALLOY ELECTRODE

A special alloy, prepared by adding 10% Pt to the Pd-25% Ag alloy and rolling to 0.001 in. foil*, is reported** to have higher corrosion resistance to nitric acid attack than either Pd-25% Ag or pure Pd. The special alloy was tested, therefore, to determine its feasibility for use as a hydrogen diffusion electrode in conjunction with a HNO_3 cathode. Foils of the special alloy were cleaned in the same manner as for the Pd-25% Ag electrodes, plated on both sides with Rh black, and oxidized for two hours in air at 600°C . Tests under four sets of conditions (Table 7) showed that the material is not a promising anode under the conditions of the tests. The reasons for the poor performances were probably low occlusion or low permeability of hydrogen, since low limiting currents were obtained at small overpotentials.

*J. Bishop Co., Malvern, Pennsylvania

**Wise, E. A., U. S. Patent 2,129,721

Table 7

ANODIC POLARIZATION OF THE PLATINUM-PALLADIUM-SILVER
DIFFUSION ELECTRODE IN ACID ELECTROLYTE

<u>Test No.</u>	<u>Electrolyte</u>	<u>Fuel</u>	<u>OCP vs SCE</u>	<u>Temperature °C</u>	<u>Results</u>
1	5M H ₃ PO ₄	N ₂ H ₄	-0.30	Room Temp. 50	No current up to 0.24 v vs OCP. A limiting current 1.6 ma/cm ² at 1.1 v vs OCP.
2	5M H ₃ PO ₄	H ₂ gas	-0.23	Room Temp. 60	Max. current 72 ma/cm ² at 0.58 v vs OCP. Max. current 80 ma/cm ² at 0.78 v vs OCP.
3	5M H ₃ PO ₄ + 0.2M HNO ₃	H ₂ gas	-0.18	Room Temp.	A limiting current 22 ma/cm ² at 0.28 v vs OCP. No improvement with temperature increase.
4	5M H ₂ SO ₄ + 0.2M HNO ₃	H ₂ gas	-0.09	Room Temp.	A max. current 10 ma/cm ² at 0.19 v vs OCP.

Foils of the same alloy were then tested as a hydrogen diffusion electrode in 5M KOH electrolyte. A foil was heated in air for 2 hours at 850°C. The open-circuit potential (OCP) of the electrode vs the hydrogen electrode potential was 0.9 volt after purging with hydrogen gas for 150 minutes. This inactive electrode was then reheated in air for two hours at 700°C. The electrode then had an OCP of 0.02 v (vs HE) and withstood 62 ma/cm² anodic polarization at an overpotential of 0.5 v (vs HE).

A foil treated for 2 hours in air at 700°C and then for 2 hours in air at 500°C withstood 38 ma/cm² at an overpotential of 0.5 volt. Another foil treated for 2 hours in air at 700°C and then for 2 hours in air at 400°C, where platinum oxide can be formed, withstood 82 ma/cm² at the same overpotential.

This series of tests indicated that the Pd-Ag-Pt alloy has a similar capability for occlusion and diffusion of hydrogen as Pd-25% Ag. Since the Pd-Ag-Pt alloy has a better resistance to acid than Pd-25% Ag, utilization of the Pd-Ag-Pt alloy as a hydrogen diffusion electrode in acid systems cannot be overlooked if a HNO₃-resistant foil is required for fuel cell application.

F. EFFECT OF SULFUR DIOXIDE GAS IN OXIDATION ATMOSPHERE

1. Background

Hatfield (ref. 13) reported a 10% increase in the oxidation rate of mild steel and a 50% increase in the oxidation rate of 18-8 stainless steel by adding 2% SO₂ to the air. Hatfield also found that the SO₂ increased the oxidation rates even more if water vapor was also added to the air. Evans (ref. 14) attributed this effect to the introduction of excess cation vacancies in the oxide film by sulfur ions. Wise (ref. 15) reported that palladium was severely attacked by H₂S gas above 600°C and, more moderately, by SO₂ gas up to 1000°C.

In the present program, SO₂ was chosen to attempt a moderate increase of the oxidation rate of palladium with the object of improving the palladium-hydrogen anode.

2. Electrode Preparation

Two Pd-25% Ag foils were annealed for two hours in argon at 800°C, plated with Rh black, and then oxidized in air containing about 15.5% (by volume) of SO₂ for two hours, one at 600°C and another at 700°C (Specimen Nos. 1 and 2). Three other foils were prepared by heating in a SO₂ atmosphere and plated with Rh as indicated in the footnote of Table 8.

3. Anodic Polarization Tests

Anodic polarization data of control Pd-25% Ag electrodes are compared in Table 8 with those of electrodes that were Rh plated and heated in SO₂.

Table 8

ANODIC CURRENT DENSITIES, ma/cm^2 , FOR Pd-25%Ag ELECTRODES
HEAT TREATED IN SO_2 GAS OR IN AIR CONTAINING 15.5% SO_2 GAS

Electrode: 0.001-in. Pd-25%Ag oxidized in SO_2
containing air.
Electrolyte: 5M KOH
Fuel: H_2 gas
Temperature: 25°C

Specimen No. §§	OCP* v	Overpotential vs HE**, volts				
		0.1	0.2	0.3	0.4	0.5
1	0.20	-	0.7	0.3	--	--
2	0.02	13	20	29	41	31
3a	0.83	-	-	-	-	-
3b†	0.00	9	14.5	19	21.5	26
4‡‡	0.00	3.8	8.0	12.8	17.5	23
5§	0.00	3.3	4.5	6	8.6	13

* Open Circuit Potential vs HE.

** Hydrogen electrode potential in the same solution
and at the same temperature.

† The current increased sharply after 0.6 volt vs HE
and the electrode withstood $400 \text{ ma}/\text{cm}^2$ at 1.24 volts vs HE.

‡‡ Reached the limiting current, $96 \text{ ma}/\text{cm}^2$, at 0.87 volt vs HE.

§ The current increased sharply beyond 0.5 volt and the
electrode withstood $400 \text{ ma}/\text{cm}^2$ at 0.94 volt vs HE.

§§ Specimen 3a: Heated in pure SO_2 for two hours at 850°C .
Specimen 3b: Rh black plated on both sides of the foil and
heated in pure SO_2 gas for two hours at 850°C .
(Specimen 3a was used again after the polariza-
tion test.)

Specimen 4: Rh black plated on both sides of the annealed
foil and heated in pure SO_2 gas for 2 hours at
 850°C .

Specimen 5: Rh black plated on both sides of the annealed
foil and heated in pure SO_2 gas for two hours at
 850°C and subsequently for two hours at 700°C .

4. Discussion and Conclusions

Specimens 1, 2, and 3 (Table 8) showed formation of heavy greyish black film when treated in air containing SO₂ gas or in pure SO₂ gas, showing the formation of oxide, sulfide, or most likely a mixture of both. Both palladium and silver were probably attacked by SO₂ gas.

Although the increase of oxidation rate might suggest the increase of cation vacancy sites or excess anions in the oxide (with sulfide) film, according to the Wagner mechanism, the polarization data indicated a definite poisoning of hydrogen uptake to the foil and the electrode reaction by treatment with SO₂ gas. It was also observed that the surface film (rhodium plating on specimens Nos. 4 and 5) fell off during the polarization tests, indicating the poor bonding between the foil and the film.

G. SUBSTITUTION OF MORE STABLE OXIDES FOR PALLADIUM OXIDE AS A HYDROGEN TRANSFER CATALYST IN PALLADIUM FOIL

1. Background

Although PdO has been shown to be an active catalyst for the transfer of hydrogen in Pd-25% Ag foils, the oxide is slowly reduced by the hydrogen, and over a ten-hour period, the capacity of the foil as an anode is destroyed. Rhodium oxide, which is more stable than PdO, was chosen as a substitute for PdO as a hydrogen catalyst. Finely divided rhodium is reported to oxidize most rapidly at about 800°C (ref. 16). On the other hand, PdO decomposes above 790°C (ref. 17). Consequently, if a Pd-25% Ag foil plated with Rh is heated above 790°C, the Rh, but not the Pd or Ag, would be oxidized.

2. Electrode Preparation

A Pd-25% Ag electrode was pretreated by (1) annealing in argon at 850°C, (2) rhodium-plating on both sides by the conditions of Table A-1 (Appendix), (3) oxidation in air at 850°C, and (4) rapid cooling in air.

3. Anodic Polarization Tests

The anodic polarization data are shown in Table 9.

Table 9

ANODIC POLARIZATION OF RHODIUM PLATED
Pd-25% Ag FOIL, OXIDIZED AT 850°C
Electrolyte - 5M KOH Fuel - H₂ gas
Temperature - 25°C

<u>Current Density</u> <u>ma/cm²</u>	<u>Potential vs HE*,</u> <u>volts</u>	<u>Current Density</u> <u>ma/cm²</u>	<u>Potential vs</u> <u>HE*, volts</u>
0	0.02	175	0.40
23.5	0.10	240	0.50
56.0	0.20	300	0.60
110	0.30	400	0.69

*HE = Reversible hydrogen potential at same pH and temperature

After the polarization data were collected, the current was kept constant at 400 ma/cm², and the electrode potential was recorded. The temperature of the electrolyte increased to 49°C within 30 minutes, reached 55°C after about 4 hours, and then stayed approximately constant. The electrode potential gradually shifted overnight to less noble values and became constant at 0.57 v \pm 0.04 v vs HE. The electrolysis was discontinued after 104 hours without any degradation of the electrode. However, the electrode failed to resume the same good performance after it was exposed to air for about four hours during the interruption of electrolysis. The electrode carried 9 ma/cm² at 0.12 v and reached a limiting current of 20 ma/cm² at 0.31 v, although the OCP was 0.03 v.

4. Thermal Reactivation of Electrode

A thermal reactivation of the above electrode by heating for 2 hours in air at 850°C fully rejuvenated the electrode. The electrode showed the similar polarization curve as that by the previous active condition up to 400 ma/cm². The electrode was tested again for longevity at 250 ma/cm² at 60°C. The potential was 0.35 v in the beginning, leveled off to about 0.5 v after 3 hours until about 300 hours were reached, and then very gradually decreased to 0.66 v until the test was stopped at 336 hours (14 days). A duplicate electrode was made and was operated at 60°C at 400 ma/cm² for 18 hours. The potential shifted from 0.80 v to 0.65 v. The operation was continued further at 250 ma/cm² for 120 hours, and the potential shifted from 0.62 v to 0.82 v. Those potentials of the duplicate were somewhat larger than that of the first one.

5. Electrode Improvement

Further improvement was made in two ways:

- (1) Oxidation in air by two steps after rhodium black plating, 2 hours at 850°C, and 2 hours at 700°C. This process introduces not only rhodium oxide but also palladium oxide, which has better polarization characteristics. (The $\frac{d \log I}{dE}$ slope is steeper.)
- (2) Oxidation in O₂ instead of air to increase the activity. Cation vacancy concentration is proportional to the 1/6 power of the O₂ partial pressure as was described in the previous quarter's report.

Anodic polarization data on these electrodes (Table 10) showed better characteristics than that of an electrode oxidized only at 850°C in air. The specimen with treatment (1) above was tested at 60°C at 250 ma/cm². The potential was 0.39 v in the beginning, leveled off to about 0.6 v for over 200 hours, and gradually increased to 0.8 v

Table 10

ANODIC POLARIZATION OF Pd-25%Ag ELECTRODE
WITH RHODIUM OXIDE

Electrode: 0.001-in. Pd-25%Ag foil plated with rhodium,
about 1 mg/cm², and oxidized.

Electrolyte: 5M KOH

Temperature: 25°C

<u>Heat Treatment</u>	<u>OCP*</u> <u>v</u>	<u>Overpotential vs HE**, volts</u>				
		<u>0.1</u>	<u>0.2</u>	<u>0.3</u>	<u>0.4</u>	<u>0.5</u>
2 hours at 850°C and 2 hours at 700°C in air	0.00	29	64	140	220	310
2 hours at 850°C in oxygen gas	0.00	44	73	125	195	270

* Open Circuit Potential vs HE.

** Hydrogen electrode potential in the same solution
and at the same temperature.

at the end of the test (336 hours). The second specimen with treatment (2) was tested at 250 ma/cm² at 90°C. The potential leveled off quickly to 0.56 v and showed no further change during the test for 336 hours.

6. Discussion

The life of an activated Pd-25% Ag diffusion electrode was prolonged from ten to more than 336 hours by using rhodium oxide as a principal catalyst instead of PdO, although the polarization was somewhat greater than that of electrodes activated by PdO, particularly at higher current densities. This improvement may be due to a slower reduction rate of rhodium oxide than palladium oxide by hydrogen. Furthermore, higher and more prolonged activity was introduced by oxidizing in pure oxygen instead of in air. This result suggested the further possibility that many p-type oxide films might be active as catalysts for the diffusion electrode.

Interruption of the test and exposure of the electrode to air destroyed the hydrogen permeability of the electrode. This result might be attributed to the following reasons: (1) hydrogen existing as a screening proton while the electrode was active changed to a more stable form such as a type of hydride and prevented further hydrogen transport, (2) oxygen from air diffused into the palladium lattice, formed a water molecule, and prevented further activity as a diffusion electrode. However, the true reason for this destruction by interruption is not understood.

Thermal reactivation restored the hydrogen permeability and the activity retained during the test for 336 hours.

These series of tests were most encouraging for the development of a palladium-hydrogen diffusion electrode that will operate continuously with high current drain and good potential.

H. EFFECT OF CONDITIONS OF RHODIUM PLATING ON ANODIC POLARIZATION OF Pd-Ag DIFFUSION ELECTRODE

Rhodium was selected for this study because we have studied the foils with rhodium plating more extensively than others and those electrodes have been revealed as one of the most promising. Conditions studied included the electrolyte type to give different types of plating (shiny and black), the deposition current density, and the deposit thickness.

1. Electrolyte

Two types of electrolyte were tested. One was a commercial Rh plating solution* giving a shiny deposit and the other was 0.01M rhodium chloride solution of pH 1 giving a Rh black deposit.

*Rhodex by Sel-Rex Co.

Approximately 1 mg/cm² of Rh was plated on both sides of a foil that was previously annealed at 850°C in an argon atmosphere. The foil plated with Rh was then oxidized (activated) at 850°C for 2 hours in air. Two plating cathode current densities, 10 ma/cm² and 125 ma/cm², were tested for each electrolyte.

Table 11 shows the anodic current densities of Pd-25% Ag diffusion electrodes at various overpotentials vs the standard hydrogen electrode. Results indicate that the electrodes with rhodium black plated from 0.01M RhCl₃ solution supported a current at least 10 times higher than that of an electrode with shiny Rh plated from Rhodex solution, although all electrodes gave the same open circuit potential.

Results also indicated that the foils plated at the higher current density gave higher anodic current at the same overpotentials than that by foils plated at the lower current density.

2. Cathode Current Density for Plating

Approximately 1 mg/cm² of Rh black was plated on both sides of Pd-25% Ag foils under various cathode current densities from 0.01M RhCl₃ solution of pH 1, and anodic polarization characteristics of these foils were determined.

Heat treatment of the foils was the same as those in the previous section, i.e., annealing at 850°C before plating and oxidation at 850°C after plating. However, during this series of tests, tabulated in Table 12, a few electrodes, particularly those plated at 250 ma/cm², showed poor activity. One of those electrodes (Test No. 5 in Table 12) was then reheated to 700°C and run again for the anodic polarization tests. Results indicated a slight improvement in the anodic current density at an overpotential of 0.1 v and more significant improvement at higher overpotentials. This improvement in di/dE slope perhaps suggests that the palladium oxide is a better catalyst than rhodium oxide for the process.

3. Effect of Amount of Plated Rh on Electrode Performance

Pd-25% Ag foils were plated with various amounts of Rh black from 0.01M RhCl₃ solution at the same current density, 125 ma/cm², which gave one of the best results among the previous tests on the effect of current density for plating. The pH of the plating solution was adjusted to 1 with HCl except for one foil, which was plated from a solution that had been adjusted to pH 2 (Test No. 3 in Table 13).

Foils were annealed in argon at 850°C before plating and oxidized in air at 850°C for two hours and further in air at 700°C for two hours. Results on anodic polarization of these foils are given in Table 13.

Table 11

ANODIC CURRENT DENSITIES, ma/cm², OF Pd-25%Ag DIFFUSION
ELECTRODE WITH RHODIUM PLATING FROM DIFFERENT PLATING BATHS

Electrolyte: 5M KOH

Fuel: H₂ gas

Temperature: Room Temperature

Test No.	Plating Bath	Cathode Current Density for Plating ma/cm ²	Weight of Rh Deposit mg/cm ²	OCP* v	Overpotential vs HE**, volts				
					0.1	0.2	0.3	0.4	0.5
1	Rhodex	10	1.2	0.00	1.4	3.8	7.4	11.0	13.2
2	Rhodex	125	0.9	0.00	5.2	9.8	17.0	25.0	36.0
3	.01M RhCl ₃	10	1.1	0.00	52	92	124	158	175
4	.01M RhCl ₃	125	1.0	0.00	56	112	178	221	270

* Open Circuit Potential vs HE.

** Hydrogen electrode in the same solution
and at the same temperature.

Table 12

ANODIC CURRENT DENSITIES, ma/cm^2 , OF Pd-25%Ag DIFFUSION ELECTRODE
WITH RHODIUM BLACK PLATED AT VARIOUS CURRENT DENSITIES,
AT VARIOUS OVERPOTENTIALS

Electrolyte: 5M KOH
Fuel: H_2 gas
Temperature: Room Temperature
Plating Bath
for Rh Black: 0.01M RhCl_3

Test No.	Cathode Current Density for Plating ma/cm^2	Weight of Rh Plated mg/cm^2	OCP* v	Anodic Current Densities, ma/cm^2 , at Various Overpotentials (η)**				
				0.1	0.2	0.3	0.4	0.5
1	10	1.2	0.00	52	92	124	158	175
2	30†	0.6	0.00	29	59	103	165	240
3	50	1.0	0.00	60	112	170	210	240
4	125	1.0	0.00	56	112	178	221	270
5a	250	0.8	0.00	26	44	56	70	82
5b	250	1.0	0.00	22	40	58	75	86
5c	250†	1.0	0.00	25	55	110	176	250
5d	250††	4.3	0.00	39	77	120	175	215

* Open Circuit Potential vs Hydrogen Electrode in the same solution and at the same temperature, HE.

** Hydrogen Overpotential vs HE.

† 5c: The electrode for the tests 5b was reheated to 700°C in air for 2 hours.

†† Oxidized at 850°C and further at 600°C in air.

Table 13

ANODIC CURRENT DENSITIES, ma/cm^2 , ON Pd-25%Ag ELECTRODES
WITH VARIOUS AMOUNTS OF RHODIUM BLACK

Electrode: 0.001-in. Pd-25%Ag foil Rhodium plated
and oxidized.

Fuel: H_2 gas

Electrolyte: 5M KOH

Temperature: Room Temperature

Test No.	Amount of Rh Black mg/cm^2	OCP* v	Overpotential (η) vs HE**, volts			
			0.1	0.2	0.3	0.4
1	0.26	0.00	44	108	215	308
2	0.50	0.00	52	110	210	315
3	0.53†	0.00	33	76	152	260
4	1.00††	0.00	56	112	178	221
5	1.60	0.00	57	126	222	315
6	3.76	0.00	57	138	240	315

* Open Circuit Potential vs HE.

** Hydrogen electrode potential.

† pH of RhCl_3 solution was adjusted to 2.

†† Oxidized only at 850°C , listed previously in Table 12.

Results indicate no significant effect as a result of different amounts of Rh deposit. Current densities on the electrode plated from the pH 2 electrolyte were somewhat lower than those plated from pH 1 electrolyte.

Since the electron-probe analysis showed that sufficient diffusion of Pd into rhodium takes place during oxidation, even at 700°C, the insignificant effect of the amount of Rh deposit is believed reasonable.

4. Conclusions

These series of tests on Rh plating suggest the following conclusions:

- (1) Rhodium black plating is more favorable than Rh smooth plating.
- (2) The maximum activity is obtained by Rh black plated at cathodic current densities of 50-125 ma/cm².
- (3) The amount of Rh deposit has an insignificant effect in a range from 0.26 to 3.76 mg/cm².
- (4) Deposit from the electrolyte adjusted to pH 1 gives better results than that from one adjusted to pH 2.
- (5) Palladium oxide is a better catalyst than rhodium oxide.

I. LIFE TEST OF THE Pd-25% Ag DIFFUSION ELECTRODE

Continuous polarization tests of several Pd-25% Ag electrodes were conducted for periods up to two weeks to test the durability of electrode activity. For these tests, the anodic current was kept constant, and the electrode potential was intermittently measured. The cell temperature was kept constant within $\pm 5^{\circ}\text{C}$ by controlling current through a heating tape that was wrapped around the cell. The results obtained to date, summarized in Table 14, indicate that the most stable electrode is one plated with Rh and heat treated in air or oxygen at a temperature high enough to form rhodium oxide. However, the better potential value was obtained from the electrode that was also treated at the lower temperature where PdO could be formed.

The electrodes plated with thin Ni or Pt and oxidized showed excellent polarization characteristics in the beginning of the test, but died out before the end of the two-week period. The reason for a short life of the electrodes with Pt may be attributed to reduction of PdO and PtO by hydrogen, but the failure of the electrode with NiO must be caused by some other factor, such as plugging of Ni ion vacancy sites by stable hydrogen ions, since NiO is believed to be very stable.

Table 14

DURABILITY OF ELECTRODE ACTIVITY

Electrolyte: 5M KOH

Fuel: H₂ gas

Specimen No.	Electrode Preparation	Temp. °C	Current Density ma/cm ²	Time hr	Overpotential vs HE*, volts		
					Start	Level	End
1	Rh plating on both sides. Heat in air for 2 hr at 850°C	60	250	336	0.35	0.50 ±0.05	0.66
2a	Same as 1.	60	400	18	0.65	0.65	0.82
2b	Continuation of 2a.	60	250	120	0.62	±0.05	0.82
3	Rh plating on both sides. Heat in air for 2 hr at 850°C, for 2 hr at 700°C.	60	250	336	0.39	0.65 ±0.05	0.82
4	Same as 3.	90	250	284	0.18	0.60 ±0.05	0.80
5	Same as 3	90	250	336	0.52	0.50 ±0.05	0.62
6	Rh plating on both sides. Heat in O ₂ for 2 hr at 850°C.	90	250	336	0.56	0.50 ±0.05	0.55
7†	Pt plating on both sides. Heat in Ar for 2 hr at 850°C, for 2 hr at 700°C.	90	250	48	0.35	0.50 ±0.05	-

Notes at end of table

Table 14 (continued)

DURABILITY OF ELECTRODE ACTIVITY

Specimen No.	Electrode Preparation	Temp. °C	Current Density ma/cm ²	Time hr	Overpotential vs HE*, volts		
					Start	Level	End
8†	Pt plating on both sides. Heat in air for 2 hr each at 850, 700 and 400°C.	90	250	<24	0.50	-	-
9††	Pt plating on fuel side and Rh plating on electrolyte side. Heat in air 2 hr each at 850, 700 and 400°C.	90	250	146	0.41	0.40 ±0.10	0.43
10†	Zr-Ni plating on both sides. Heat in Ar for 2 hr at 850°C, in air for 2 hr at 700°C.	90	250	48	0.73	0.70	-
11†††	Ni plating on both sides. Heat in Ar for 2 hr at 850°C, in air for 2 hr at 700°C.	90	250	240	0.51	0.65 ±0.10	0.57
12†††	Ru plating on both sides. Heat in Ar for 2 hr at 850°C, in air for 2 hr at 700°C.	90	250	175	0.75	0.80 ±0.05	0.80

Notes at end of table

Table 14 (continued)

DURABILITY OF ELECTRODE ACTIVITY

Specimen No.	Electrode Preparation	Temp. °C	Current Density ma/cm ²	Time hr	Overpotential vs H ₂ *, volts		
					Start	Level	End
13†	Heat in Ar for 2 hr at 850°C, in air for 2 hr at 700°C. Then Ru plating on both sides. Heat again in air for 2 hr at 700°C.	90	250	48	0.58	0.50 ±0.05	0.54

* Hydrogen electrode potential in the same solution and at the same temperature.

† Died out during the night.

‡ Died out as Rh plating dropped off.

‡‡‡ Died out by suddenly evolving oxygen. The potential turned instantaneously to the oxygen evolution potential, about 1.7 volts vs HE.

J. GENERAL CONCLUSIONS

- (1) Characteristics of the alloying elements that strongly affect the anodic polarization of Pd-25% Ag diffusion electrode include valency of the elements and thermal characteristics of hydrogen occlusion.
- (2) Effects by alloying elements were independent of the side on which the electrode was plated.
- (3) Alloying elements that improved the electrode performance most significantly included:

Fuel side:	Pt, Ir, and Co
Electrolyte side:	Rh, Ir, and Ni-Zr
Both sides together:	Pt, Rh, and Ir
- (4) The structure type of an oxide (whether the n- or p-type) is the property that most strongly affects the anodic polarization characteristics of a Pd-25% Ag foil when the oxide is applied to the surface of the foil.
- (5) Some of the best oxides to improve the electrode were:

Fuel side:	Th, Cu, Ru, and Mg
Electrolyte side:	Ni, Pt, and Rh
Both sides together:	Pt, Rh, Ru, and Ni
- (6) Metallographic examination and electron microprobe analyses indicated that the diffusion rates of alloying elements varied widely so that alloys of some elements were satisfactorily prepared while other elements failed to alloy.
- (7) Pd-25% Ag, alloyed with 10% Pt, showed the similar capability for occlusion and diffusion of hydrogen as Pd-25% Ag, so the Pt alloy can be used in a proper acid electrolyte system containing HNO_3 because of its favorable resistance to oxidizing acids.
- (8) SO_2 gas in an oxidizing atmosphere poisoned the Pd-25% Ag electrode.
- (9) Pd-25% Ag electrodes oxidized in pure O_2 showed better performance than those oxidized in air.
- (10) Substitution of PdO by rhodium oxide (perhaps Rh_2O_3) as a catalyst prolonged the life of the Pd-25% Ag electrode more than 30 fold.
- (11) The best electrode, both in terms of life and anodic polarization characteristics found to date, is prepared by the following process: Full annealing, Rh black plating, and oxidation in pure oxygen at 850°C (perhaps followed by the further oxidation at 700°C in oxygen).

(12) The best Rh plating is accomplished by the following procedure:

Electrolyte:	0.01M RhCl_3 solution, pH 1
Cathode current density:	50 125 ma/cm ²
Amount of Rh deposit:	more than 0.5 mg/cm ² up to approximately 3 mg/cm ²

K. FUTURE PLANS

Planning for the coming quarter includes the following:

- (1) Continue life tests on electrodes treated in various ways suggested during the present quarter.
- (2) Utilize hydrazine or other storable fuel on Pd-25% Ag diffusion electrode.
- (3) Study acid electrolyte system with Pd-25% Ag diffusion electrode.
- (4) Attempt to combine Pd-25% Ag diffusion electrode with various oxygen electrodes to make a full cell.

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APPENDIX

A. PHASE DIAGRAMS OF ALLOYING METALS WITH PALLADIUM

Ag, Cu, Ni, Fe, Co, Pt, Ir, and Rh, with Pd: A continuous series of solid solutions is formed (Ir-Pd has not yet been studied; however, they likely make an unbroken series of solid solutions since both have face centered cubic structure and very similar lattice parameters.) Cu and Fe have ordered structures at lower temperatures in some concentration ranges.

Pd-Li, Pd-Th: Not known

Pd-Mg: The c/a ratio of the Mg hexagonal lattice is slightly decreased by adding Pd because of an increment of the a parameter of Mg, although the atomic radius of Pd is smaller than that of Mg.

Pd-Sn: Several intermetallic compounds, including a partially filled As-Ni structure at around 40 atomic-% Sn. The solid solubility of Sn in Pd (α phase) was estimated to be about 9.5 atomic-% Sn.

Pd-Ru: Cannot form a continuous series of solid solutions because of different lattice structure. Otherwise, not well known.

Pd-Al: Not very well investigated. However, three intermetallic compounds are known. There is almost no solubility of Pd in the Al-rich range, and Pd forms a solid solution at about 25 atomic-% Pd.

Pd-Ti: Form several intermediate phases.

Pd-Zr: Preliminary experiments showed that the lattice of Pd is expanded by Zr.

B. PREPARATION OF ALLOY FOILS

The alloying of all elements except Li with Pd foils consisted of the following steps:

- (1) Degreasing with trichloroethylene and acetone.
- (2) Chemical cleaning with warm chromic acid cleaning solution.
- (3) Plating of alloying metal by electrolysis or by vacuum evaporation.
- (4) Diffusing into the Pd surface by heating for two hours at 850°C in an argon atmosphere.

(5) Oxidizing in air for two hours at 650°C.

Plating conditions for metal deposition are summarized in Table A-1. The plating time was sufficient to deposit approximately 5 mg/cm² of metal in each case, so that if all metal diffused into the surface, the foil contained approximately 10% of the metal.

Lithium was deposited as LiO by heating the foil in argon for two hours at 850°C, then in air for one hour at 700°C. The foil was then dipped into saturated Li₂CO₃ solution, dried in air, and heated in air for ten minutes at 700°C. The treatment with Li₂CO₃ solution was repeated three times.

Other metals, Mg, Ti, Zr, Th, Zr-Ni, and Ni-Cr, are being deposited on palladium foil by vacuum evaporation*. Because of the nature of the evaporation method, the amount of these metals and alloys were very small. After four to ten cycles of metal evaporation, the weight increase of the foil was 0.01 to 0.1 mg/cm².

C. ELECTRON MICRO-PROBE ANALYSES (REF. 19)

Some recording charts of electron micro-probe analyses of particular interest for characterizing alloyed and heat treated Pd foils are shown in this section (Figures A-1 to A-8). Since the thin foils were mounted in the sample holders at various angles with the face of the holder, the cross sectional true distance of the foil is shown on the charts as a micron (μ) scale. The digit "0" at the bottom of an arrow indicating the concentration of each element indicates the ground level for each measurement. The concentration of Pd can be read downward from the top edge, and the concentrations of plated metals can be read upward from the bottom edge in these figures. The middle lines in the figures indicate the total intensity of the counting. Since various analyzing crystals were used for the analyses, and since the curves were recorded on various counting scales, metal concentrations as indicated by these curves cannot be directly compared. On each figure, the approximate scale for the concentration of each element and the original interface between the foil and the plated layer are indicated.

The following analyzing crystals were used for each element:

Mica - Pd, Rh, and Ru
LiF - Pt
Quartz- Ni, Co, and Fe

* Model JEE-4V Vacuum Evaporator, Japan Electron Optics Laboratory, Japan.

Table A-1

CONDITIONS FOR ELECTRO-PLATING Pd-25% Ag ELECTRODES

<u>Metal</u>	<u>Solution</u>	<u>Approximate pH</u>	<u>Current Density ma/cm²</u>	<u>Temperature</u>
Ag	AgNO ₃ : 40 g/l HNO ₃ : 4 g/l, NaNO ₃ : 75 g/l		15	40°C
Cu	CuSO ₄ ·5H ₂ O: 80 g/l H ₂ SO ₄ : 150 g/l		90	R.T. ⁺
Ni	NiCl ₂ : 13 g/l, NH ₄ Cl: 20 g/l, NaCl: 10 g/l	6.0	45	R.T.
Fe	FeCl ₂ ·4H ₂ O: 24 g/l KCl: 180 g/l	5.5	25	R.T.
Co	Co(NH ₄) ₂ (SO ₄) ₂ ·6H ₂ O: 175 g/l, As ₂ O ₃ : 0.1 mg/l	5.5	50	R.T.
Su	SnCl ₂ ·2H ₂ O: 3 g/l NaOH: 100 g/l		50	R.T.
Pt	H ₂ PtCl ₆ : 25 g/l Pb(C ₂ H ₃ O ₂) ₂ : 0.3 g/l	1 (HCl)	30	R.T.
Ir*	H ₂ IrCl ₆ : 4.1 g/l	1 (HCl)	50	R.T.
Rh	RhCl ₃ : 2.1 g/l	1 (HCl)	300	R.T.
Ru	RuCl ₃ : 2.1 g/l	1 (HCl)	300	R.T.

*Before electroplating, the Pd-25% Ag foil was treated to obtain an adherent Ir black plating. The foil was dipped into saturated iridium chloride solution and heated in a gas flame to yellow heat. This treatment was repeated three times. + RT = Room Temperature

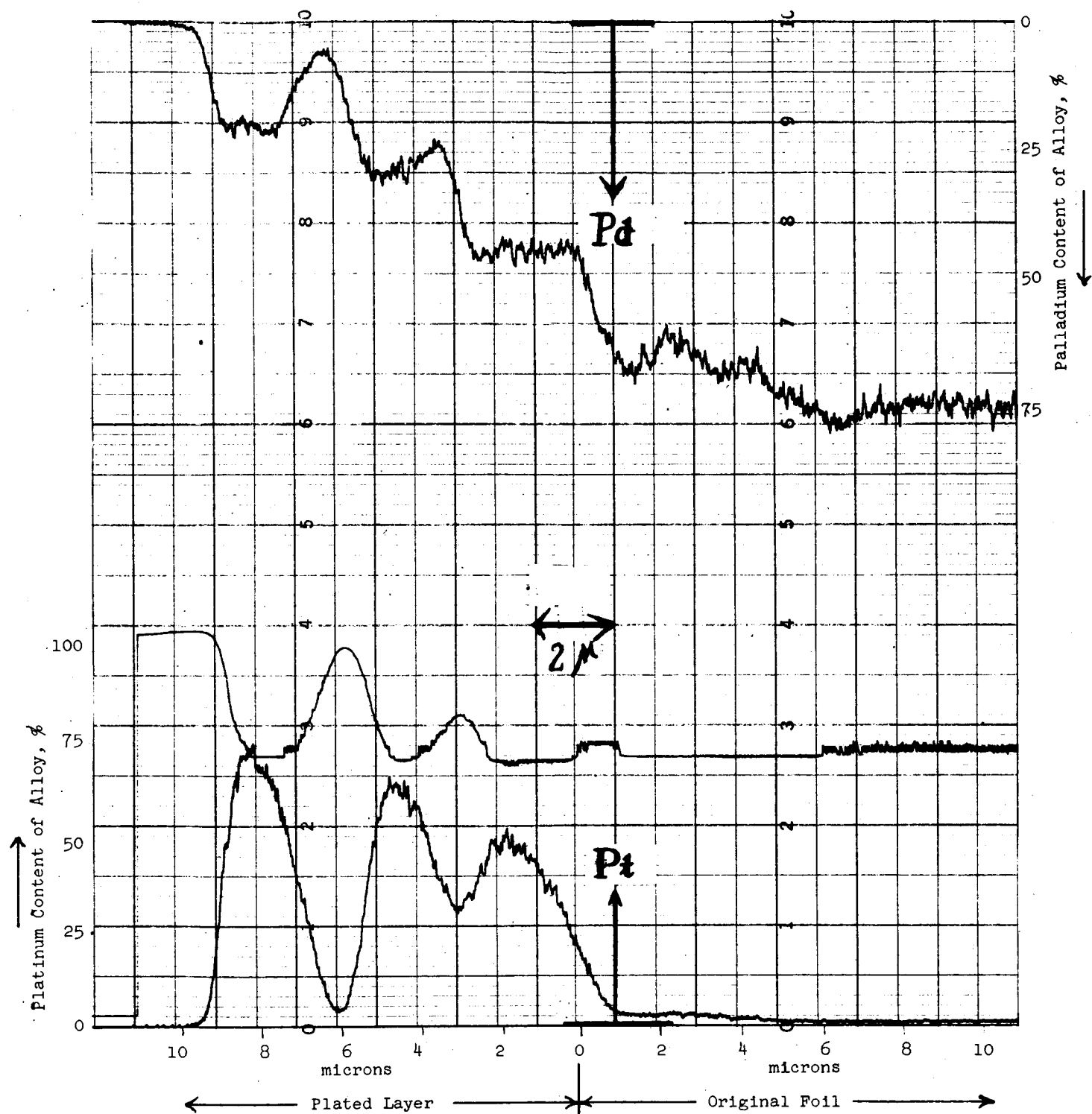


Figure A-1. Cross section of the diffusion layer of Pt into Pd-25% Ag (diffusion treatment in argon for 2 hr at 850°C). Maximum points on both concentrations indicate the powdery Pt deposit.

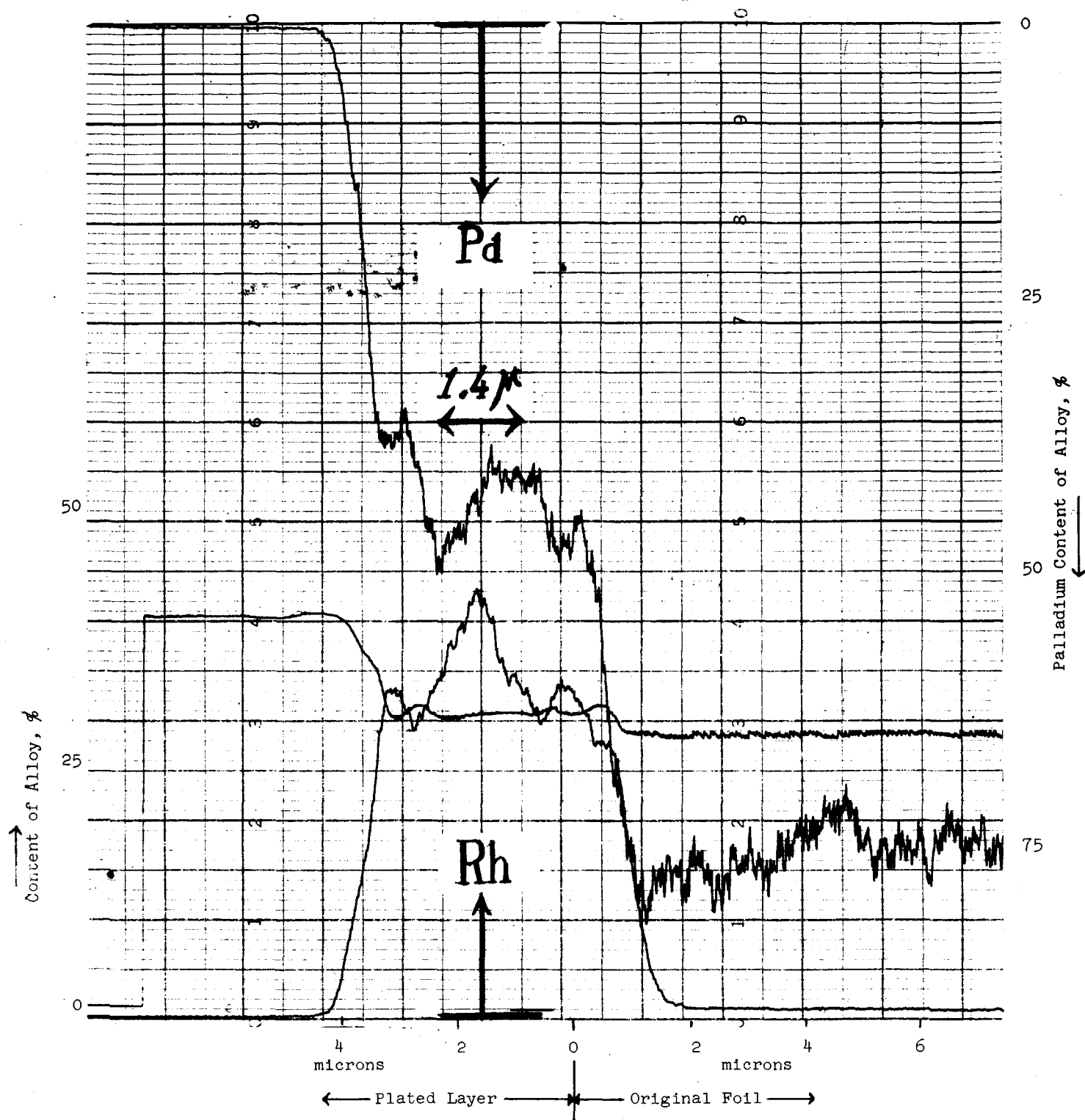


Figure A-2. Cross section of the diffusion layer of Rh into Pd-25%Ag (diffusion treatment in argon for 2 hr at 850°C).

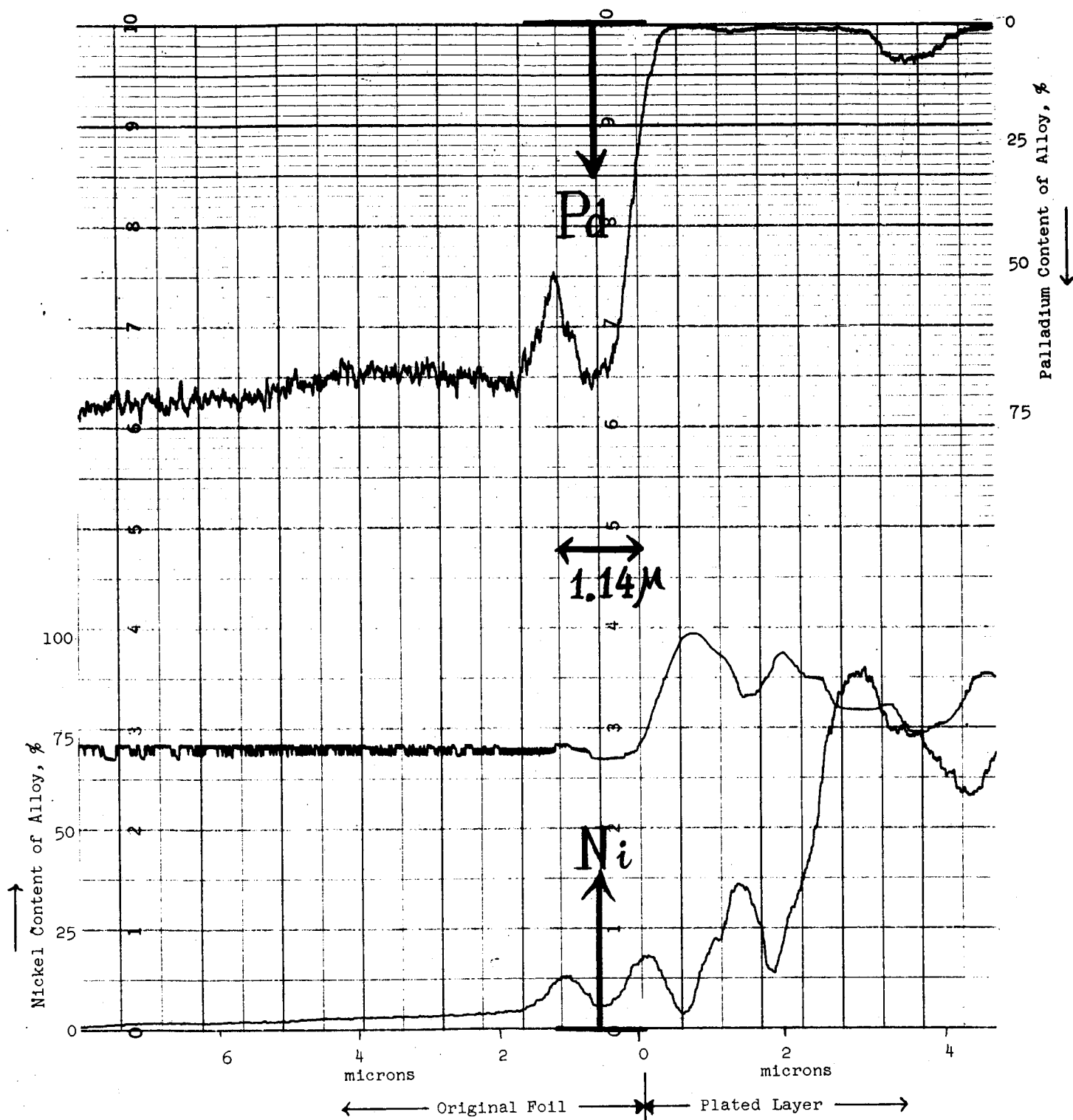


Figure A-3. Cross section of diffusion layer of Ni into Pd-25%Ag (diffusion treatment in argon for 2 hr at 850°C). A small valley on the Pd curve indicates a heavy diffusion of nickel at the palladium grain boundary.

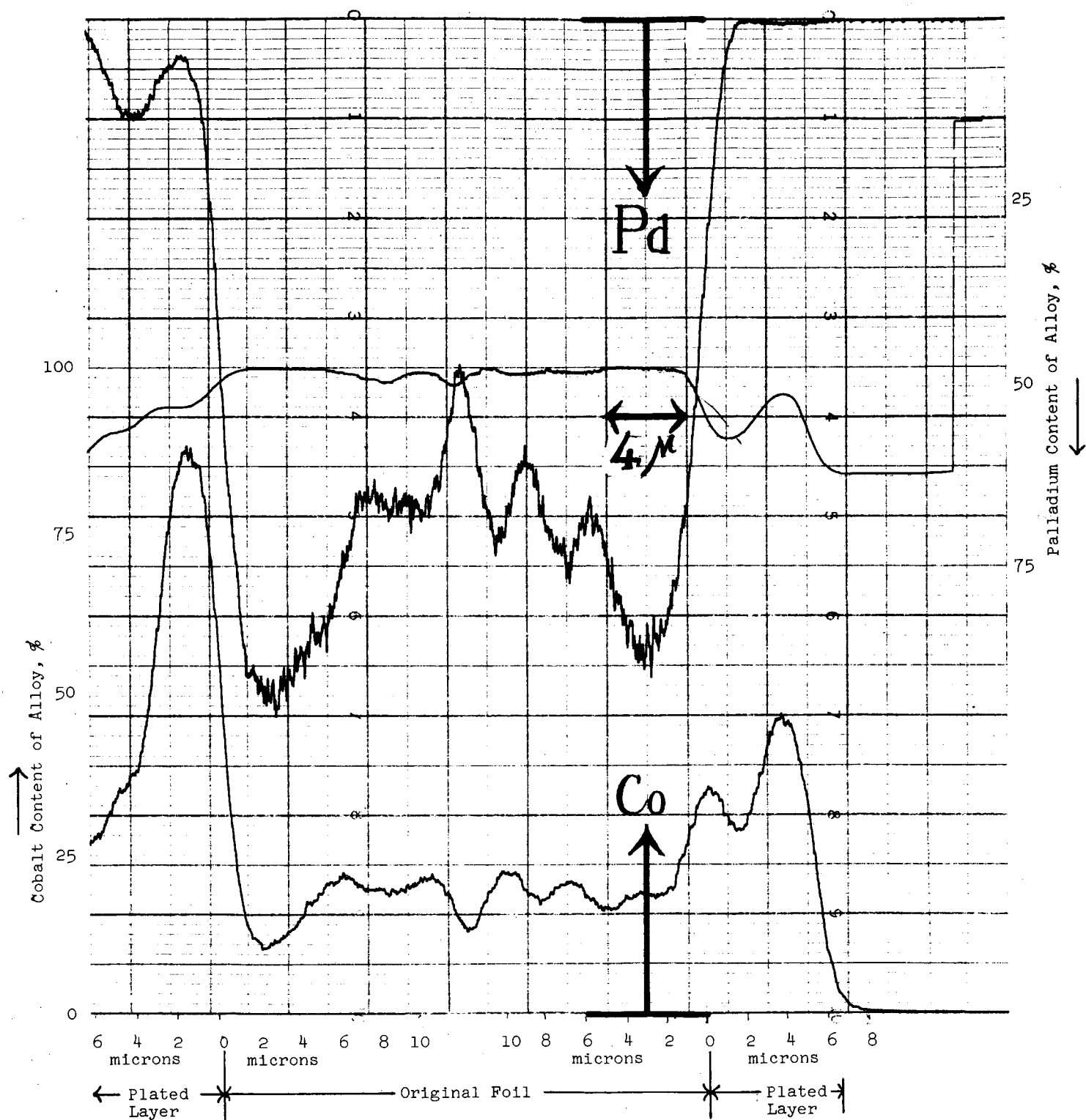


Figure A-4. Cross section of Pd-25%Ag foil alloyed with Co by diffusion treatment in argon for 2 hr at 850°C.

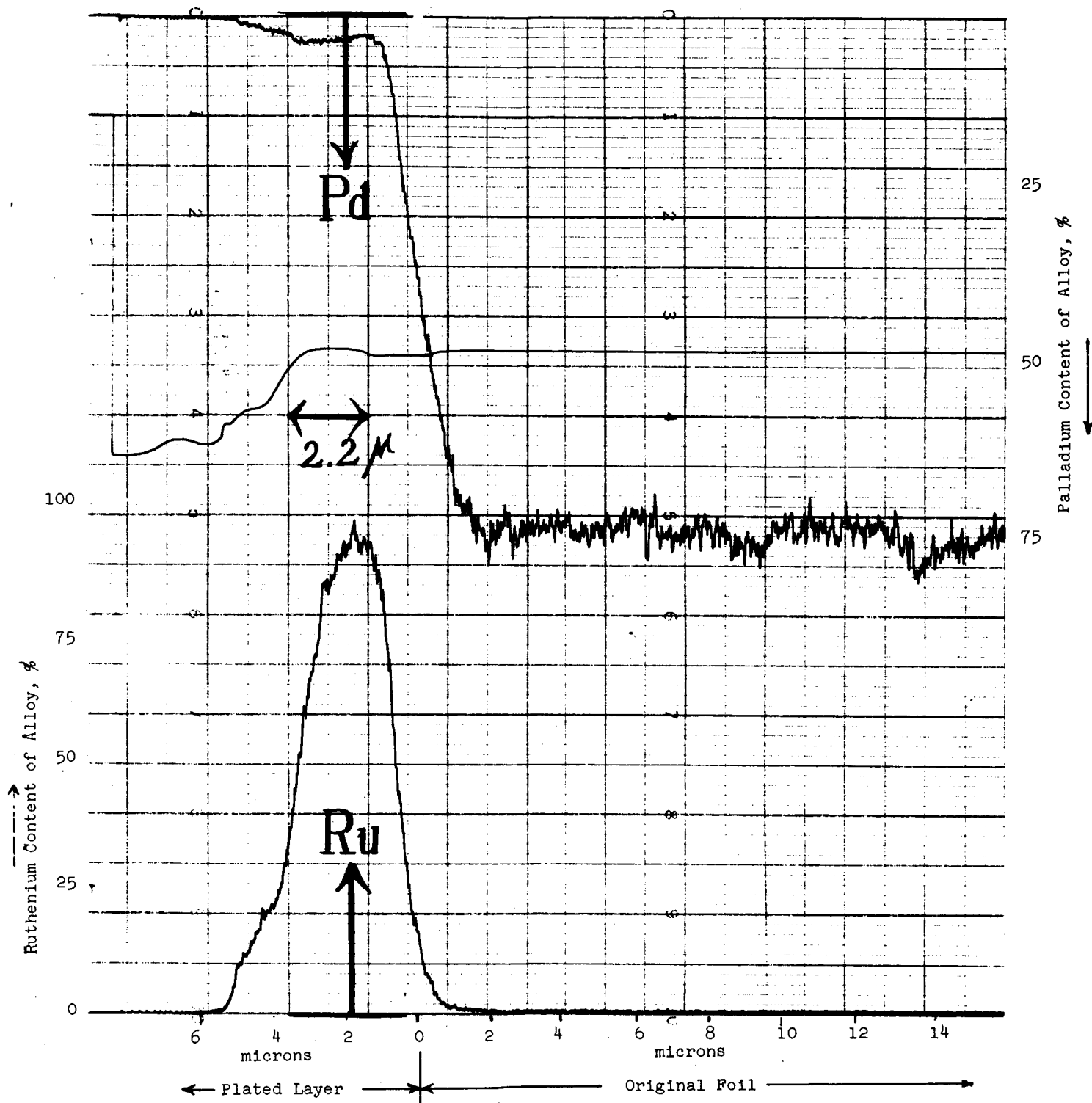


Figure A-5. Cross section of the diffusion layer between Ru and Pd-25%Ag (diffusion treatment in argon for 2 hours at 850°C).

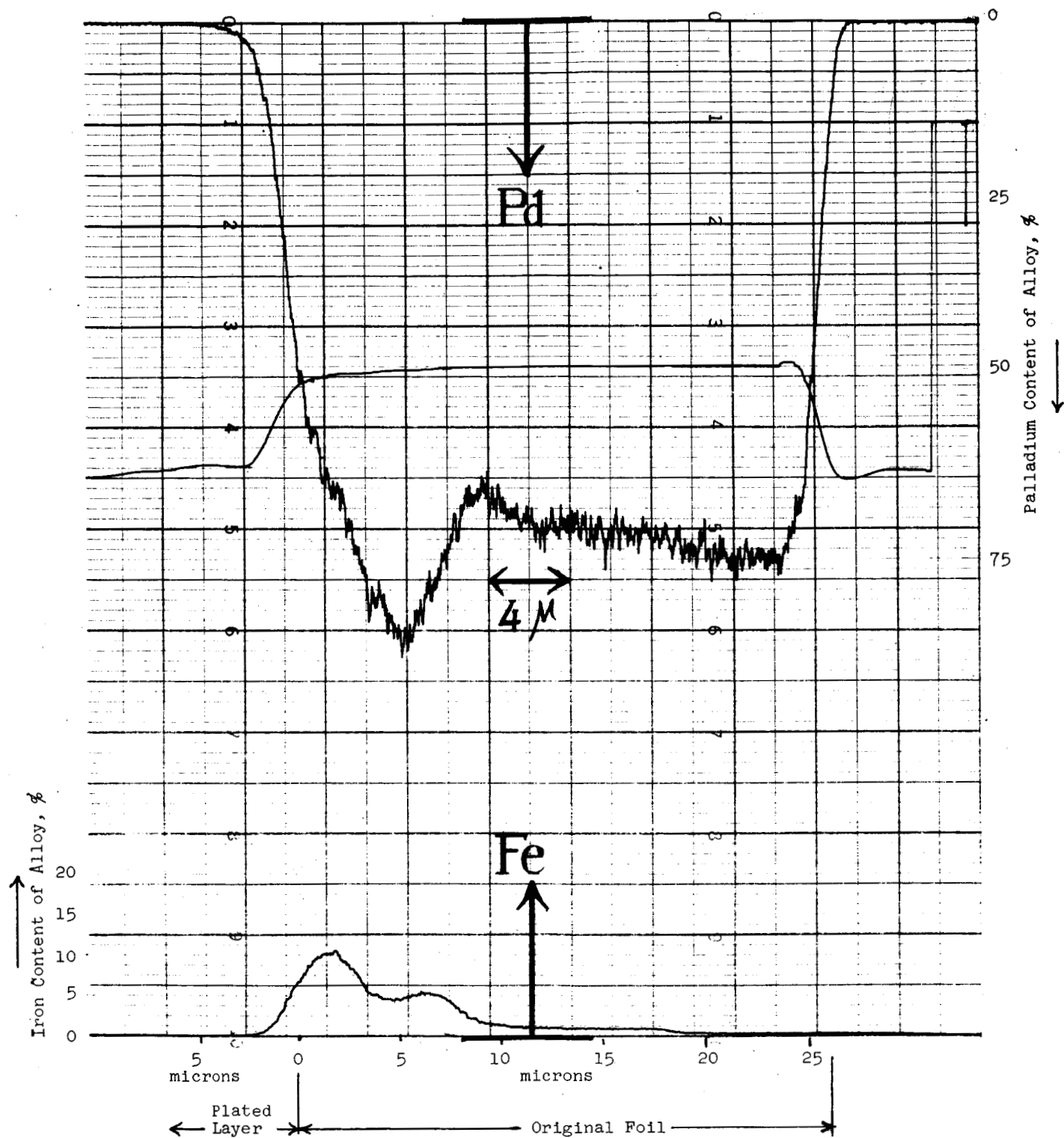


Figure A-6. Cross section of Pd-25%Ag foil diffused through by Fe plated on one side (diffusion treatment in argon for 2 hours at 850°C).

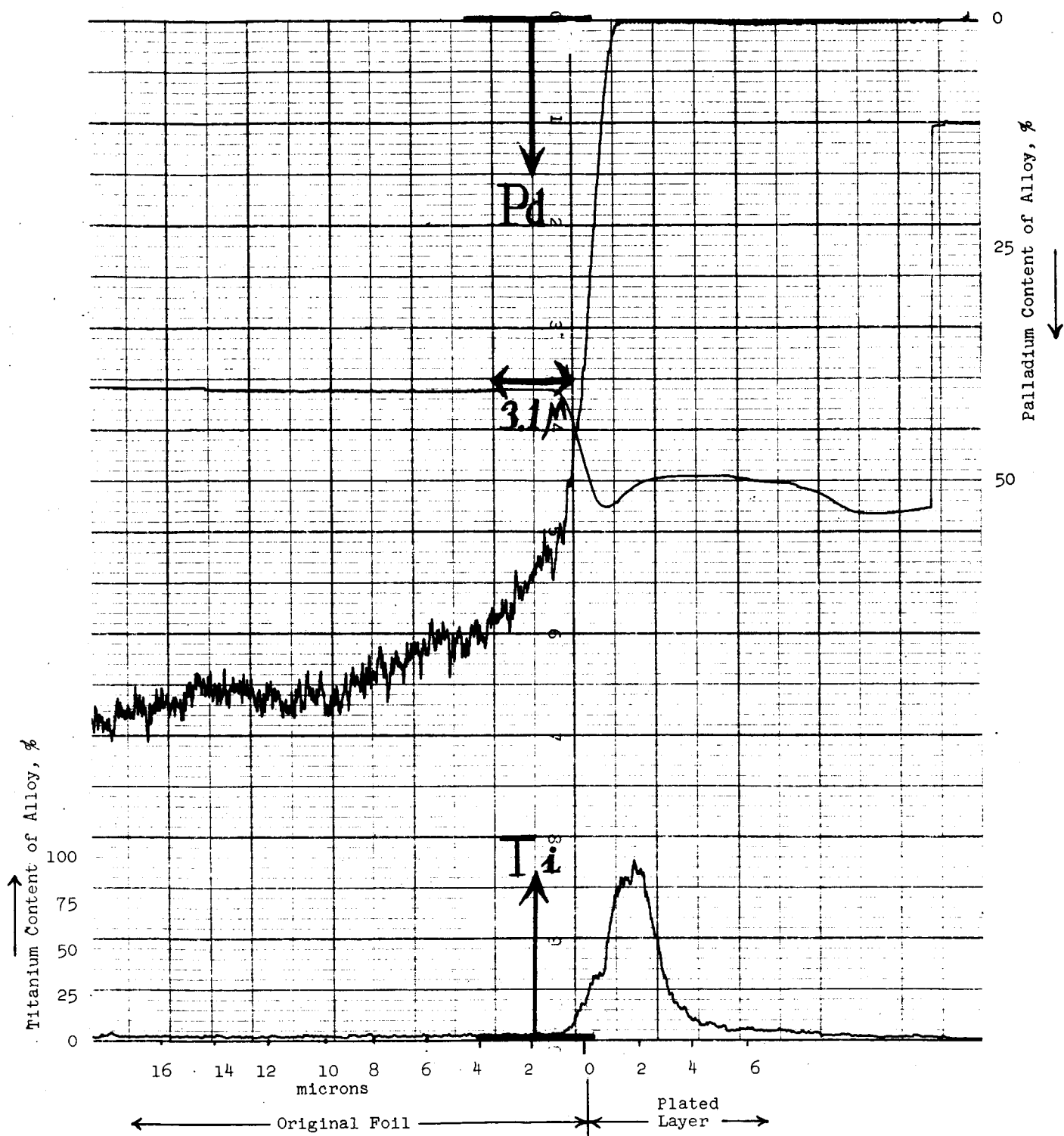


Figure A-7. Cross section of diffusion layer between Ti and Pd-25% Ag (diffusion treatment in argon for 2 hr at 850°C).

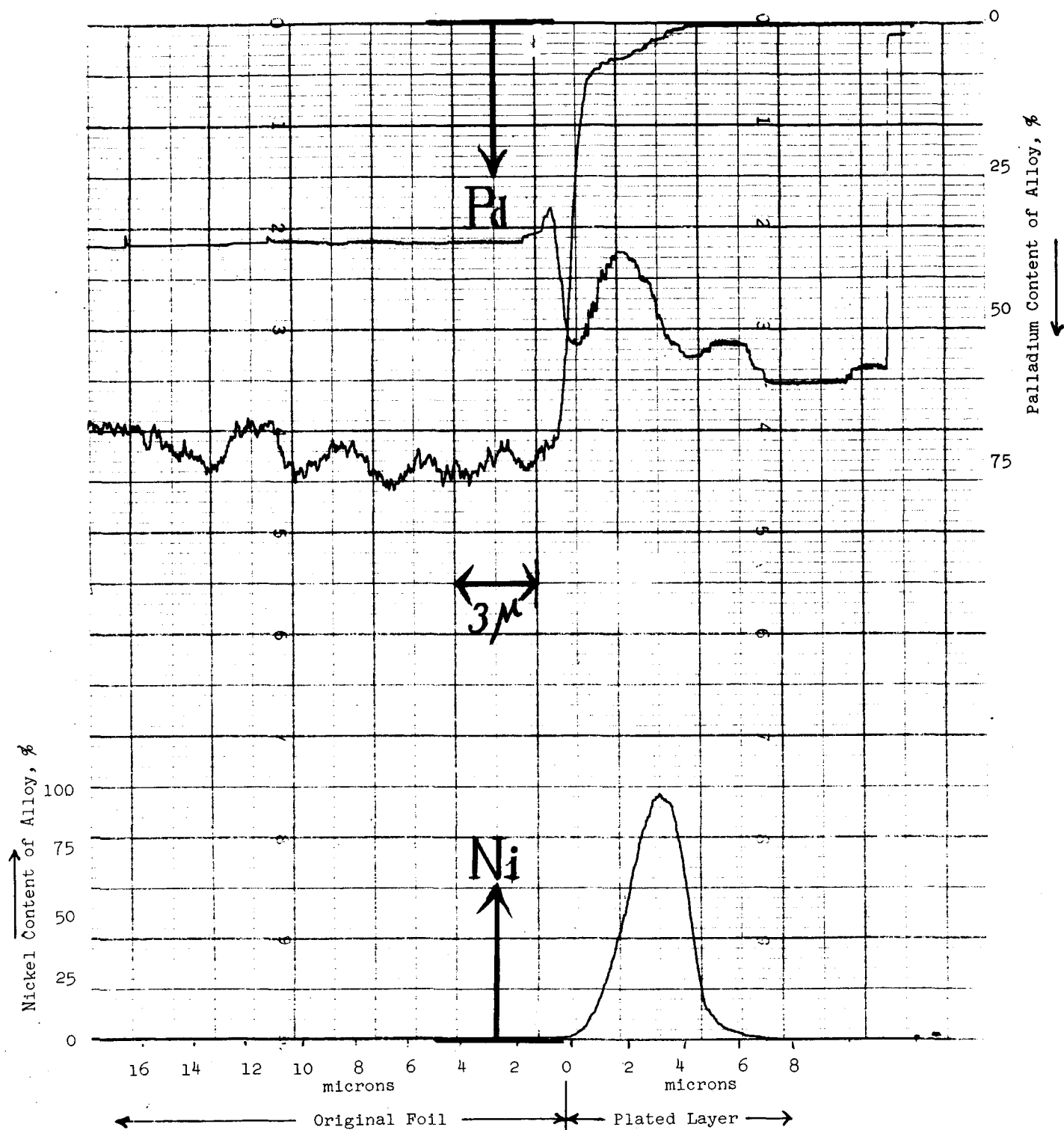


Figure A-8. Cross section of Pd-25%Ag foil plated with Ni (no diffusion treatment, oxidation in air for 2 hr at 700°C).